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A STUDY OF INCORPORATING HEAVY OIL AND SYNTHETIC CRUDE RESIDUA INTO FLUID CATALYTIC CRACKING FEEDSTOCKS

FINAL REPORT
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OBJECTIVE

The overall objective of this proposal is to evaluate the viability of producing transportation fuels from heavy oil and synthetic crude residua by incorporating these materials into fluid catalytic cracking feedstocks. Yield data obtained by microactivity testing along with established modelling procedures will allow an assessment of these feedstocks in the fluid catalytic cracking unit operation.

The specific objectives of this proposal are:

1. to establish microactivity test yield data for residua with metal-tolerant catalysts

2. to determine the effect of metals and metal passivators on yields with these catalysts

3. to assess through modelling whether these feestocks, catalysts and passivators will lead to a viable fluid catalytic cracking operation.

JUSTIFICATION

With long term rising oil prices and a national objective of becoming self-sufficient in crude oil production in spite of declining conventional reserves, Canadian refiners must process greater amounts of residual materials in conventional oil and treat the high proportion of residua in Western Canadian heavy oils. Of particular importance is the conversion of these low value residuals into high value transportation fuels. Currently, in most integrated refineries, atmospheric tower bottoms are fractionated by vacuum distillation into a vacuum gas oil, which is further processed, and a vacuum tower bottoms which is blended into residual fuels such as bunker oils or converted to asphalt. Conversion of vacuum tower bottoms into transportation fuels would produce a higher value product, eliminate the surplus of bunker fuels in Eastern Canada and meet the nation's goal of oil self-sufficiency.

Presently, vacuum gas oils are catalytically cracked into gasoline and cycle oils in fluid catalytic cracking units (FCCUs). The processing of atmospheric tower bottoms, which contain both vacuum gas oil and vacuum tower bottoms, in these units would have the potential of converting residua to transportation fuels. This option is attractive since no capital investment is required as most refineries have FCC units. However, high metals content in the atmospheric tower bottoms (ATB), as well as their relatively high concentration of coke precursors, have mitigated against using ATBs as FCCU feedstocks. The presence of metals leads to excessive catalyst consumption and other operating problems. With a new generation of metal-tolerant catalysts, along with the development of metal passivators, catalytic cracking of residua as a component of FCCU feedstocks has become a viable processing alternative and has been investigated in this report as a low cost upgrading option relevant to the Canadian refiner.

BACKGROUND AND USEFULNESS

The fluid catalytic cracking unit (FCCU) is a key operation in the modern oil refinery [1]. The unit converts high molecular weight feeds, such as gas oils, to lower molecular weight transportation fuels (e.g. gasoline), distillate and coke. This processing is essentially a carbon rejection operation whose produced coke keeps the unit at cracking temperatures and in thermal balance. This unit operates by contacting the feed at high temperature with a catalyst which promotes cracking and reduces the molecular weight of the feedstock by carbon-carbon bond cleavage. The catalyst is separated from liquid product and recirculated to a regenerator where deposited coke is burnt off with air, producing heat to keep the FCCU in thermal balance and reactivating the catalyst. The unit operation is a delicate balance between endothermic cracking and exothermic combustion which can be upset by components of the feedstocks such as metals (Ni and V) and coke forming precursors. Excessive feed metals content will lead to a build-up of metals on the catalyst causing a loss of catalyst activity. Excessive coke formation, which results in high regenerator temperatures, may not be operationally feasible or may cause excessive catalyst degradation As a result, feeds containing high metal and coke precursor concentrations have been avoided in practise. Furthermore, catalytic cracking has been optimized to produce gasoline from gas oils. Projected fuel consumption trends call for a decrease in gasoline demand but a marked increase in middle distillate requirements; therefore, these studies should optimize, if possible, the yield of these middle distillates.

With increased need for residua conversion, better metal- and temperature-tolerant catalysts have been developed which allow for the catalytic cracking of conventional atmospheric tower bottoms (ATB). ATBs from Canadian crudes such as Lloydminster heavy oil present particular processing problems due to their very high metals and coke precursor contents. ATB from both conventional and heavy oils will provide problems with catalyst poisoning by metals and excessive coke production. Fluid catalytic cacking unit data (yields and operating conditions) for these materials have been compared with that from conventional Canadian FCCU feedstocks so that the viability of cracking residua can be assessed.

Syncrude ATB is quite atypical in that it is bottomless (no vacuum residua) and has a low metals content. Since there is no residua (540+) fraction, Syncrude ATB is essentially a gas oil. Catalytic cracking of this material is problematic because it is a hydrotreated cracked stock and is unique compositionally due to a high content of stable aromatic and polyaromatic species. Syncrude ATB or gas oil, will not be as detrimental to catalytic activity as conventional ATBs, but it will be far less amenable to conversion by catalytic cracking because of its composition. Deep hydrogenation of conventional feeds have allowed an evaluation of the effect of feedstock composition on catalytic cracking yields. These materials have ranged from Waxy 80N, a material containing a large proportion of cycloparaffins, to Slack Wax, which is largely paraffinic in nature. MAT product yields for these feeds have been compared to those of the aromatic Syncrude gas oil to assess the effects of composition on yields. In practise, effecting such compositional changes without a molecular weight reduction may be difficult; however, MAT data show the resulting effect such changes can have on cracking yields.

Fluid catalytic cracking unit data can be estimated for any feedstock using a combination of microactivity testing, modelling and experience. The microactivity test catalytically cracks a feedstock in a bench scale fixed-bed reactor swept with nitrogen. Reactor effluents are analyzed to produce yield data for feeds at particular operating conditions. Yield data with conventional fluid catalytic cracking feedstocks from the microactivity test can be related to commercial operations to produce differences in the commercial and laboratory scale units. These differences can be applied to microactivity tests with nonconventional feeds or catalysts to estimate commercial yields. Slight modelling of these yield structures is required to estimate a fluid catalytic cracking unit's operation because the MAT is an adiabatic, once-through reactor. As a result, when these critera are imposed, overall unit yields change slightly. When all these variables are considered, the viability of ATBs as fluid catalytic cracking feedstocks can be assessed.

The work in this contract has studied atmospheric tower bottoms as a feedstock for fluid catalytic unit operations. Advanced metals-tolerant catalysts and a metals passivator have been evaluated by determining MAT yields experimentally for these materials with both conventional and synthetic crude ATBs. This data, along with MAT data for conventional gas oils, provides an experimental basis for estimating commercial yields of transportation fuels from nonconventional FCCU feeds.

EXPERIMENTAL

The experimental program carried out in conjunction with this contract can be divided into six distinct areas. These include: 1) Feedstock Evaluation, 2) Catalyst Evaluation, 3) Catalyst Impregnation, 4) Microactivity Test, 5) Microactivity Test Data Reduction, and 6) Statistical Analysis of MAT Data. Each of these experimental procedures, as they were conducted for the purposes of this work, is described in the following.

1) FEEDSTOCK EVALUATION

Fluid catalytic cracking feedstocks are characterized by a number of physical and compositional properties determined by generally accepted and standarized methods [2]. The physical properties determined include: specific gravity, aniline point, viscosity, Conradson carbon content, asphaltene content, penetration, as well as nitrogen, sulphur and metals concentrations and normal boiling range.

Specific gravities for all materials were determined in a Paar Densitometer at specific temperatures such that the material was a liquid. The specific gravity was then corrected to 60°F by standard correlation tables. The densitometer measures specific gravity on the basis of an oscillating tube filled with liquid. Specific methodology is outlined in ASTM Method D4052-81. The specific gravity, once determined, can be converted to the API gravity by the following relationship:

$$°API = (141.5/s.g.\ @\ 60°F) - 131.5$$

Specific gravity increases or API gravity decreases with increased residua content and/or aromatic content in a feedstock.

Aniline point is another standard ASTM method (D611) which measures the temperature of miscibility of aniline with an equal volume of liquid hydrocarbon sample. The aniline point is a rough measure of the paraffin content of the sample since it increases with paraffin concentrations, assuming all factors such as molecular weight and boiling range are equal.

The viscosity for all feeds was measured with a Zeitfuch pipette at 100°C. Viscosity increases with the molecular weight and the boiling range of the material analyzed. This method is also a standard industry procedure outlined in ASTM D445.

The Conradson carbon determination is used to measure a material's propensity for forming coke. The experimental procedure employed was a modification of ASTM D189 in that an Alcor MiniConradson carbon analyzer was used. This instrument produces superior results because it employs both a nitrogen gas blanket and an automatic programmed temperature profile. As a result, analytical data is both more precise and reproducible.

Asphaltene contents of residua were obtained by the method ASTM D3279. This analysis relies upon the insolubility of high molecular weight heteroaromatic species in a normal paraffinic solvent. Contact of the sample with the solvent precipitates asphaltenes which are determined gravimetrically. The asphaltene level is dependent on the molecular weight of the n-paraffinic solvent and decreases with increasing molecular weight to heptane where it becomes constant with an increasing of solvent carbon number.

Metals analyses, particularly nickel and vanadium, are another very important factor in assessing FCCU feedstocks. The metals are found in all crude oils, generally as prophyrin complexes, and because they are high molecular weight species they occur in the gas oil and particularly the residual fractions. Feedstocks are analyzed for metals by combustion in a platinum dish followed by washing the combustion residue with isooctane onto a Millepore filter. The filter cake is then sandwiched in a plastic cell and metals are determined by x-ray fluorescence.

Pen is a conventional asphalt determination, ASTM D5, which determines the penetration of a standard needle into a sample at a given temperature. The degree of penetration, along with the temperature are an indication of the "heaviness" or refractory nature of the sample. Distillate pens cannot be measured since the materials are not true solids at the temperature of measurement.

Gravity, aniline point, asphaltene content, viscosity, Conradson carbon residue, and pen, when taken together and compared with other similar feedstocks, are an indication of the refractory nature or heaviness of the feedstock. In elemental terms, the heavier a feedtock becomes, the more hydrogen deficient it becomes and as a result gravity, asphaltene content, viscosity and Conradson carbon residue increase. Pen, on the other hand, decreases.

Nitrogen and sulphur levels are important variables in fluid catalytic cracking due to their effect on catalysts, product quality and stack gas emissions from the regenerator and associated boiler. High nitrogen contents in FCCU feeds, in excess of 1000 ppm, have been known to cause catalysts to lose activity. This has generally been attributed to basic nitrogen compounds which bind to Lewis acid sites during cracking, causing the loss in activity. High sulphur contents are also deliterious to product quality, since the significant amounts of sulphur contaminate FCCU liquid products. More importantly, organic sulphur and nitrogen are oxidized in the regenerator to form their respective oxides, which can present the refiner with pollution problems. Since the sulphur levels in most feedstocks are an order of magnitude greater than nitrogen levels, they present the greatest pollution problem. For the materials evaluated in this work, sulphur has been determined by x-ray fluorescence with a PGT-100 instrument, while nitrogen has been analyzed by both microcoulometric and Kjeldahl methods. Gas oils were determined by the former method as outlined in ASTM D3431, while residua were assayed with the classical Kjeldahl technique which reduces the feed nitrogen to ammonia with sulphuric acid and a selenium catalyst (ASTM D3228).

All feeds were analyzed for normal boiling range by a gas chromatographic simulated distillation, as described in ASTM D2887. The method consists of injecting a liquid sample into a temperature programmable gas chromatograph equipped with an 18" x 1/4" dia. 10% OV-101/Chromasorb P column and an FID detector. The instrument is calibrated for retention time and true boiling point with a blend of n-paraffins which cover the boiling range of the sample to be determined. The instrument produces a chromatogram whose area slices are summed and normalized with respect to the total area to

report a true boiling point curve for distillates on a mass % basis. For residua the technique is modified to include an internal standard, since all of the sample will not elute due to its low vapour pressure. Residua are defined in terms of normal boiling point and are typically that portion which has a normal boiling point greater than 504°C.

Compositional analyses were obtained by mass spectrometry in conjunction with both column chromatography and/or distillation. Vacuum gas oils were evaluated with column chromatography and mass spectral analysis. The feedstocks were separated into saturate, aromatic and polar fractions on a tripart clay/silica gel/alumina column. Elution of the sample with hexane allowed the saturates to be collected at the bottom of the column while the polar and aromatic fractions were adsorbed on the clay and silica gel adsorbents, respectively. Both aromatic and polar fractions were eluted with diethyl ether and methanol. Evaporation of the solvents left saturate, aromatic and polar fractions. The former two fractions were analyzed separately on a Kratos 25Q mass spectrometer and the results, when combined with elution chromatography data, allowed the complete composition of the gas oil to be reported.

Atmospheric and vacuum tower bottoms were analyzed compositionally by distillation/precipitation/mass spectrometry and precipitation/mass spectrometry, respectively. For atmospheric tower bottoms, the sample to be analyzed was distilled (ASTM D1160) into distillate (IBP-504°C) and residual (504°C+) fractions. The distillate fraction was analyzed as a normal vacuum gas oil, as described above. The residual fraction was heptane deasphalted (ASTM D3279), and the heptane solubles were analyzed by high resolution mass spectrometry. Distillate, heptane soluble and asphaltene analyses were then combined to produce an overall compositional analysis of the ATB. Vacuum tower bottoms were analyzed in a similar manner, except the distillation of the sample into gas oil and residua fractions was omitted since it is not required.

2) CATALYST EVALUATION

Fluid catalytic cracking catalysts are evaluated by microactivity, surface area, pore volume, bulk density, elemental analysis, particle size distribution and scanning electron microscopy. The microactivity test, ASTM D3907-80, measures the amount of standard gas oil, under standard conditions which is converted to material boiling less than 216°C and coke. Fresh catalyst has very high activity (>80) and with use in operation the catalyst activity declines. Since commercial units are constantly adding fresh catalyst and withdrawing equilibrium catalyst, the refiner uses the microactivity test to measure the reactivity of the catalyst in the FCC unit. Details of the method can be found in the section on the Microactivity Test.

Fluid catalytic cracking catalysts are aluminosilicates composed of crystalline zeolites and binder. Their activity is related to both their surface area and their apparent bulk density. Surface areas were measured on a Micromeritics Surface Area Analyzer with nitrogen at liquid nitrogen temperatures. Bulk densities were determined by weighing a known volume of material. Catalyst activity is lost with time in commercial operation. Severe and sudden losses of activity are generally paralleled with large changes in surface area and/or bulk density if the cause of the lost activity is thermal or hydrothermal degradation.

Pore volume was measured on a Micromeritics Pore Volume Analyzer, Model 9300, which determines the cumulative pore volume of a solid sample by intrusion of a liquid under pressure. Mercury at hydraulic pressures up to 30 000 psig was used to measure the pore volume distribution of all equilibrium FCCU catalysts in the range 100 to 0.01 m.

Metallic impurities in the catalysts were also determined as well as the material's alumina content. Metals - nickel, vanadium, iron, copper, and sodium, were evaluated by atomic absorption spectroscopy. The analysis was the same as that described above except for sample preparation. With FCC catalysts, the sample was dissolved in a solution of hydrofluoric and sulphuric acid. This was then taken to dryness and the residue was then redissolved in 0.5N HCl. The hydrochloric acid solution was then diluted if necessary and analyzed by atomic absorption spectroscopy.

The carbon content of all catalysts used in MAT experiments was determined by combustion with a Leco Carbon Analyzer. This apparatus converted all carbon in a weighed amount of sample to carbon dioxide, which was then absorbed on ascarite and determined gravimetrically. This residual amount of carbon was used to correct the determined carbon levels on spent catalyst after MAT experiments so that the net carbon or coke generated during the MAT run could be determined and more accurate coke yields reported.

Particle Size was determined by light scattering. FCCU catalyst is a fine classified solid material which has a narrow size distribution by virtue of the unit's operation. Since the catalyst is fluidized in both the reactor dense phase and the regenerator through many cycles, coarse and fine fractions are attrited and lost, accounting for the narrow size distribution. Drastic changes in particle size distributions are indicative of mechanical problems in a commercial unit. The analysis is reported here only for completeness.

Scanning electron microscopy, with a Jeol Model 35CF SEM was employed in order to indicate the bulk physical features of equilibrium FCCU catalysts up to 10 000 X magnification. The distribution of transition metals through a cross section of a catalyst particle was also attempted with the use of a Tracor Northern Energy Dispersive Spectrometer, which allowed elemental density maps to be determined. Catalysts were prepared by gluing them to a carbon specimen mount with a carbon paint. For bulk physical features the catalysts were used as is; however, for metal distribution studies, the catalyst was gently crushed before mounting so that cross sections of particles would be available for study.

3) CATALYST IMPREGNATION

Equilibrium fluid catalytic cracking catalysts were impregnated with metal salts (Ni, V, Sb) to evaluate the effect of these elements on MAT product yields. The procedure was similar to that reported in the literature [3]. 60 g of equilibrium catalyst were placed in a beaker and slurried with a toluene solution of nickel octoate, vanadium naphthenate and Nalco N-5000 (22% Sb in light petroleum distillate) containing sufficient metals so as to impregnate the catalyst to the desired level. Typically, 500 or 1000 ppm nickel and vanadium were added both with (500 ppm) and

without antimony. The toluene solution was allowed to evaporate to dryness in a fume hood at room temperature and the resulting solid, containing adsorbed metals, was dried in an oven at 100°C.

The impregnated catalyst was then steamed at regenerator temperatures for at least eight hours in order to age the impregnated metals and produce a catalyst which would simulate commercial metals-contaminated catalyst. The steaming was carried out by charging 15-20 g of impregnated catalyst to two Vycor boats. These were then placed into a 1" diameter Vycor tube in a 1" Lindberg SB tube furnace. Air saturated with water vapour at 60°C was passed through the furnace at 10 mL/min. The furnace was then heated to 1350°F and held at that temperature for 8 to 12 hours. Three lots of impregnated catalyst were steamed and the combined product was analyzed for metals (Ni, V, Sb) and carbon and used for further MAT work.

4) MICROACTIVITY TEST

The microactivity test (MAT) was the primary experimental method used in this work. The procedure employed was a modification of ASTM D3907-80, which is a standard method evaluating FCCU catalyst activity. In the ASTM method, the gasoline yield (IBP-216°C) of a specified feed is determined under a standard set of conditions (T=482°C, C/O=4). The procedure was modified so that reactor temperature, hydrocarbon feedstock, and the ratio of catalyst to oil can be varied. For this study the WHSV was not held constant but varied only over a small range. The total MAT product range - gases, liquids and coke on spent catalyst - was determined so that a complete product yield for the MAT experiment could be calculated. These products included hydrogen, methane, LPGs, gasolines (C_5 - 220°C), light cycle oil (220-344°C), decant oil (344+°C) and coke and since they were evaluated their yield as a function of MAT operating conditions is known.

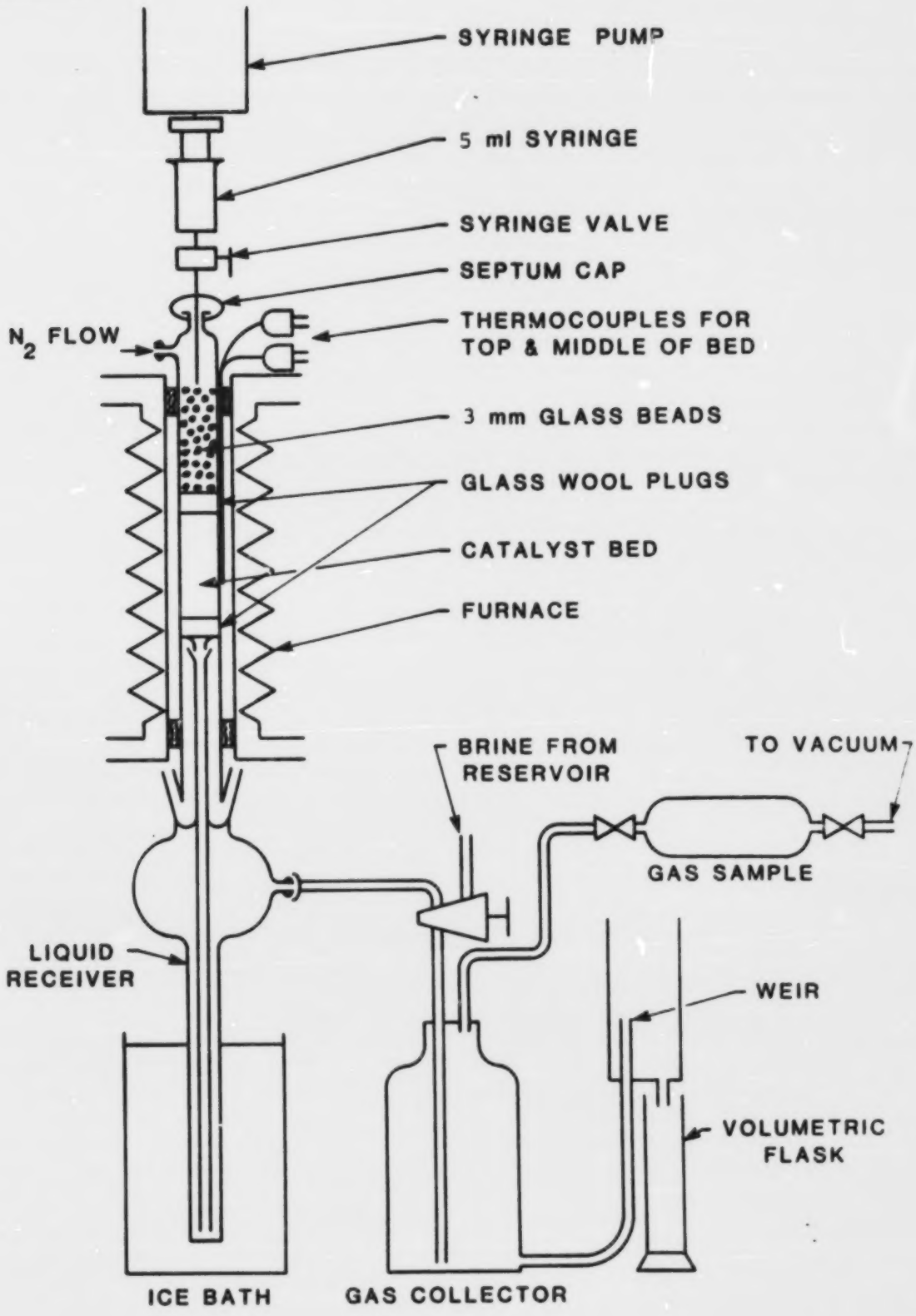
The MAT is a fixed bed downflow reactor constantly swept by an inert gas (nitrogen) during the course of the experiment. While it is operationally quite different than a commercial riser/cracker, experience and the literature [4] has shown that the directional changes in operating conditions in both units are reflected in similar changes in product yields.

A schematic diagram of the experimental apparatus is shown in Figure 1 and the procedure for operating this unit follows. A MAT reactor is a 40 cm long x 1.2 cm O.D. tubular reactor equipped with a constriction in the middle of the tube, a male B-14 ground glass joint on the reactor bottom and a septum port and a side arm for charging feed and gas to the reactor at the top. A glass wool plug is placed above the constriction and the desired amount of catalyst to be studied is weighed by difference into the reactor. A second glass wool plug is placed on top of the catalyst and sufficient 3 mm glass beads are placed on top of this plug to fill the reactor to within 5 cm of the septum. A septum cap is put into the septum port and two J type thermocouples are attached to the outer skin of the reactor such that they will measure skin temperature at both the top and mid points of the catalyst bed. The reactor is then placed in a vertical tube furnace and a nitrogen line is attached such that the flow of gas through the reactor is maintained at 20 mL/min. A manometer is also attached to the incoming gas line so that the differential pressure across the bed can be measured. The reactor is then heated to reaction temperature and a preweighed liquid receiver is connected to the bottom of the tubular reactor. The liquid receiver is immersed in an ice bath and vented through 4 mm O.D. nylon tubing to a gas collection system which has the ability to contain the entire gas stream evolved during the course of the experiment. Once the reactor has reached thermal equilibrium at the desired temperature, the nitrogen flow rate through the bed is adjusted to exactly 20 mL/min and the temperatures at the top and the middle of the bed as well as the ambient room temperature are recorded along with the pressure differential across the reactor and the barometric pressure.

The hydrocarbon feedstock to be tested is charged to a hypodermic syringe. Care is taken to exclude air and the syringe with approximately 1.1 mL of feed is weighed. It is then injected through the septum cap and the syringe pump is connected with the barrel of the syringe to begin pumping feed. When ready, the operator begins injecting feed by starting the syringe pump and timer. Simultaneously, the gas flow from the liquid receiver is diverted to a gas collection bottle. The brine in the bottle is displaced over a weir which is adjusted so that the collected gas is at room pressure and temperature. The displaced brine is collected in a 1000 mL graduated cylinder so that the total volume of gas collected can be measured. Approximately 1 mL of feed is injected over the first 100 seconds of the run. At that time, the syringe pump is stopped and the nitrogen flow is continued for another 800 seconds to strip both the reactor of liquids and the receiver of light petroleum gases. During the initial stages of the run, the maximum pressure across the MAT reactor, as well as the minimum flow rate and skin temperatures of the top and middle of the reactor bed are recorded. When convenient, the syringe is removed from the apparatus and weighed.

At the end of 900 seconds, the MAT run is complete. The gas collection system is isolated, the furnace is shut off and the liquid receiver is removed from the apparatus, dried and weighed. The liquid in the receiver is then made as homogeneous as possible and transferred to a liquid capsule bottle which is refrigerated. The liquid material is eventually analyzed by a gas chromatographic simulated distillation, as described above under Feedstock Evaluation, in order to determine the fractions of reactor effluent liquid which have boiling points of 220°C and 344°C. The total volume of brine displaced is recorded and a composite sample of the collected gas is taken with an evacuated Orsat bottle. The gas composition is then determined by mass spectrometry on an MS5 instrument. Once the reactor cools to room temperature under a flow of nitrogen, it is removed from the apparatus and the catalyst is recovered and analyzed for total carbon content. This completes the microactivity test.

Figure 1



A SCHEMATIC DIAGRAM OF THE MICROACTIVITY TEST APPARATUS

5) MICROACTIVITY TEST DATA REDUCTION

The microactivity test can give a wealth of product yield data provided the gas, liquid and solids produced during the MAT run are analyzed in sufficient detail. Furthermore, the reliability of the data obtained must be verified by closing a mass balance around the actual experimental run.

Mass balances are calculated by comparing the weight of products to that of the feed injected. The weight of injected feed is determined experimentally from the difference in the weight of the syringe before and after injection. The weight of coke is determined directly from the weight of catalyst and its carbon content before and after the MAT run. The weight of liquid generated is also determined directly from the differences in liquid receiver weight at the end and the beginning of the experiment. The direct determination of weight of gas evolved can be made from the effluent gas compositon corrected for air, water vapour and nitrogen content and the ideal gas law since the volume, pressure and temperature of the collected gas are known. When the directly determined weights of coke, liquid and gas are summed and compared with the weight of the feed injected, a mass balance expressed as a percentage of feed can be quoted. Good MAT data have mass balances in the 97-102% range. Balances in the range of 95-105% may be acceptable if the feed or the catalyst is particularly troublesome.

Since the directly determined weights of products do not necessarily equal the weight of feed, MAT product yields are made whole by assuming any discrepancies in the data are due to errors in the amount of gas determined. This results in the weight of gas being corrected in order to force a mass balance and, therefore, the relative amounts of each of the gas components are adjusted accordingly. Gasoline yields are calculated from the C_5+ gasoline components and the weight of reactor effluent liquid which boils up to 220°C. Cycle oil yields are calculated directly from GCD data and the weight of reactor effluent. These data are all reported on a mass % basis which is atypical with most of the data reported in the literature, particularly that from commercial operations which is reported in liquid volume %. Due to the very small samples of materials collected and the fact that they are not

fractionated into products, densities cannot be measured and accurate volumetric yields reported. However, the data can be converted to such yields if one is willing to assume average specific gravities for various materials. This should be done with caution.

The product yields are reported as a mass % of the feed and were calculated with the following expression:

yield ith product = (weight ith product/weight feed) X 100

6) STATISTICAL ANALYSIS OF MAT DATA

Eight sets of MAT experiments were analyzed by statistical analysis in order to obtain predictive models for coke and conversion in terms of temperature and catalyst/oil ratio. Further work was attempted on fitting individual product yields to functions of temperature and conversion. Since material balance discrepancies have been resolved, and the experiments for a particular catalyst/feed combination were conducted in a 3 x 3 factorial design, a model with linear and quadratic terms in temperature and C/O ratio plus four possible interaction terms was suggested. However, since such a model would be badly overparametrized, nothing more complicated than fitting a standard quadratic response surface was attempted, for example

$$\text{coke} = a + bT + c(C/O) + dT^2 + e(C/O)^2 + fT(C/O) + \text{error}$$

These regressions were carried out using The Statistical Analysis Data System.[+]

[+] SAS Institute Inc., "SAS User's Guide: Basics, 1982 Edition", Cary N.C., 1982

RESULTS AND DISCUSSION

The experimental program carried out in conjunction with this contract has dealt with microactivity testwork with characterized conventional gas oils, residua, unique FCCU feeds and both conventional and metals-tolerant catalysts. Work on metals impregnation and metals passivation has also been dealt with. In order to break up this data into meaningful areas of discussion, the following general topic areas have been used to present and discuss the experimental results:

1) Feedstock Characterization

2) Catalyst Characterization

3) Experimental Design

4) MAT Product Data for Catalysts and IPL VGO

5) MAT Product Data for Vacuum Gas Oils and DA-300

6) Effect of IPL VTB on MAT Product Yields

7) MAT Product Data for IPL 33.7% VTB/66.3% VGO and DA-300

8) Effect of Lloydminster ATB on MAT Product Yields

9) MAT Product Data for Lloydminster ATB/VGO and DA-300

10) The Effects of Ni/V Contamination on DA-300

11) Effect of Athabasca Bitumen on MAT Product Yields

12) MAT Product Data for 53.3 wt.% Athabasca Bitumen and 46.7 wt.% Syncrude Vacuum Gas Oil and DA-300

13) An Effect of Composition on Cracking Yield

14) Metals Passivators

15) Utility of Data

1) FEEDSTOCK CHARACTERIZATION

Three vacuum gas oils and related residua were characterized as fluid catalytic cracking feedstocks by both physical (Table 1.1) and compositional (Table 1.2) analyses. Physical properties and elemental analyses indicate that the quality of the gas oils as FCCU feedstocks was:

IPL > Lloydminster > Syncrude

This can be seen in the API gravities and aniline points which both decrease from 24.6 to 19.8 to 17.3 °API and 94.8 to 65.7 to 61.1°C for these gas oils, respectively. These data indicate that the IPL gas oil contains the greatest level of paraffins which are easily cracked in an FCCU operation. The viscosity of these feeds also decreases from IPL to Syncrude to Lloydminster.

Strict comparison of these gas oils is difficult because true boiling point data indicate they are not of the exact same boiling range. Mid range and final boiling points for the IPL gas oil are 462 and 627°C, while they are 420 and 587°C for Lloydminster gas oil and 419 and 577°C for Syncrude gas oil. This indicates that the IPL gas oil is heavier than the other two studied and this will have an effect on several physical properties since aromatics and impurities are concentrated in the heavy ends. This also likely accounts for the high Conradson carbon value of the IPL gas oil (0.78%) relative to those values for Lloydminster and Syncrude gas oils (0.04 and 0.07%, respectively).

Sulphur levels in the gas oil range from 0.49% for IPL to 2.34% for Lloydminster and 0.438% for Syncrude. This is expected since the Syncrude material has been hydrotreated and much of its initial sulphur content has been removed. Both the IPL and Lloydminster materials are straight run materials, and their sulphur contents are typical of sweet conventional and heavy crude oils.

The nitrogen contents for IPL, Lloydminster and Syncrude gas oils are 0.09, 0.05 and 0.132% respectively. IPL gas oil contains slightly more nitrogen than Lloydminster due to its higher boiling range, while Syncrude contains approximately 50% more nitrogen than either, even though it has been hydrotreated. This is due to the very large initial nitrogen levels in bitumen as well as the difficulty in hydrodenitrification.

Metals contents for both IPL and Syncrude gas oils are very low (<0.05 ppm), while the Lloydminster gas oil contains a small amount of vanadium (0.2 ppm). These concentrations are insignificant when compared to the metal levels present in the residua. However, they are important in determining the catalyst addition rates since both nickel and vanadium poison FCCU catalysts. The catalyst addition rate is related to the metal content of the feedstock by the following relationship:

$$\text{Catalyst Addition } (kg/m^3 \text{ of feed}) = \rho_{FF} \times \frac{\text{Ni equivalents in Feed } (\mu g/g)}{\text{Ni equivalents on Equilibrium Catalyst } (\mu g/g)}$$

ρ_{FF} density of fresh feed

The residual materials employed in this study follow the same quality trends as their gas oils, i.e.

IPL VTB > Lloydminster ATB (376°C+) > Athabasca Bitumen (220°C+)

This is surprising, to some extent, since the poorer quality feeds contain successively more distillate, which should dilute the residual materials. Distillation data show that the 5% and 30% boiling points of these materials are 470 and 609°C for IPL VTB, 376 and 500°C for Lloydminster ATB and 308 and 485°C for Athabasca bitumen. The data show that both the Lloydminster and Athabasca resids contain approximately 30% gas oil and distillate materials. The IPL vacuum tower bottoms contains no gas oil or distillate and yet has a much higher API gravity than the other two feeds (12.5 vs. 8.6 and 7.5, respectively).

The metals contents of these feedstocks also reflect their quality. IPL VTB contains 40.4 ppm nickel and 22.4 ppm vanadium, while Lloydminster ATB contains 63.1 ppm nickel and 136 ppm vanadium. Athabasca bitumen contains slightly more nickel, 65 ppm, and much more vanadium, 204 ppm. As a result of the very high metals contents in both Lloydminster and Athabasca residual feedstocks catalyst consumption rates as described by the above relationship will be at least 2-3 times greater.

Sulphur levels in the residua also reflect the feedstock quality. IPL VTB contains 1.06 wt.% sulphur, while Lloydminster and Athabasca residua contain 5.27 and 4.91 wt.%, respectively. The high sulphur levels in FCCU feedstocks should be avoided since they will be eventually converted to low quality liquid products, H_2S or SO_x. Nitrogen contents for all three resids are very similar, being 0.48, 0.39 and 0.42 wt.%, respectively.

Conradson carbon residues for the residua are greatest for IPL VTB and successively less for Lloydminster ATB and Athabasca bitumen. This is due to the boiling range of the feedstock and not its quality. Compositional data will clearly show IPL VTB is the superior FCCU feedstock; its high Conradson carbon content is due to its lack of volatility. This suggests that the use of Conradson carbon data to assess the quality of a feed is only a very rough guide.

Aniline point data could not be measured with residua since the interface cannot be observed with these black opaque materials. Similarly, penetration could be measured only for IPL vacuum tower bottoms, since the ATB and bitumen contained large amounts of distillate, making these materials too soft for such measurements.

Compositional data (Table 1.2) confirm the observations made from physical measurements and provide an insight into the chemical species to be converted during cracking. A comparison of IPL, Lloydminster and Syncrude vacuum gas oils shows that they have successively lower concentrations of saturates (paraffins and cycloparaffins), similar levels of monoaromatics and successively higher levels of polynuclear aromatics. These data can be used to estimate the catalytic

cracking precursors using the following relationships:

gas + gasoline = saturates + monoaromatics

light cycle oil = diaromatics + 1 ring aromatic sulphur + 2 ring aromatic sulphur + 1/2 (3 ring aromatic sulphur)

decant oil + coke = 100 - (gas + gasoline + light cycle oil)

With this as a rough guide to product yields, and assuming that gas and gasoline are the desired products, data in Table 1.2 shows that IPL gas oil is the best feedstock since it contains 77.3 wt.% gas and gasoline precursors. By this criterion, Syncrude gas oil is marginally better than Lloydminster gas oil (64.7 versus 60.9 wt.% gas and gasoline precursors). The greater level of gas and gasoline precursors in Syncrude is due to its greater concentrations of monoaromatics, even though it has fewer saturates than Lloydminster. Light cycle oil precursors for IPL, Lloydminster and Syncrude gas oils are 10.7, 20.3 and 15 wt.% respectively. This results in total precursor levels (gas + gasoline + light cycle oil) of 88.0, 81.2, and 81.6 wt.% for these materials and again suggests that IPL gas oil is the superior feedstock.

A similar comparison can be made with the residua studied. Compared to their respective gas oils, the residua contain fewer saturates, monoaromatics and diaromatics but more polyaromatics, polars, sulphur species and asphaltenes (Table 1.2). Based on the above relationships, residual materials have less liquid precursors (gas + gasoline, light cycle oil) but far more decant oil and coke precursors than their respective gas oils.

Compositional comparisons of IPL vacuum tower bottoms, Lloydminster atomospheric tower bottoms, and Athabasca bitumen parallel those of their corresponding gas oils, in spite of the fact these residua have successively lower initial boiling points. IPL VTB, Lloydminster ATB and full range Athabasca bitumen (220°C+) contain progressively lower concentrations of paraffins (6.74, 4.88 and 1.61 wt.%). Mono and condensed cycloparaffin levels are also greatest for IPL

VTB (11 and 24.1 wt.%), less for Syncrude gas oil (9.76 and 20.5 wt.%), and even less for Lloydminster ATB (9.02 and 17.8 wt.%). Since monoaromatics levels for all residua are similar, this results in gas and gasoline precursors being greatest for IPL VTB (53.4 wt.%) followed by Lloydminster ATB (44.1 wt.%) and Athabasca bitumen (41.8 wt.%). These potential yields are some 16.8 to 23.9% lower than those of the corresponding gas oil. Light cycle oil precursors are 10.9, 15.0 and 16.9 wt.% for IPL VTB, Lloydminster ATB and Athabasca bitumen. For IPL VTB and bitumen these are similar to those levels found in their corresponding gas oil. Lloydminster ATB has some 5 wt.% less LCO precursors than its gas oil, due solely to the lower diaromatics levels in the ATB. Total levels of liquid precursors for the residua are far less than for corresponding gas oils (58.7 to 64.2 wt.%) and, as a result, these materials should be expected to form more decant oil and coke.

TABLE 1.1

Physical Properties of MAT Feeds

Crude Source / Feed		IPL Vacuum Gas Oil	IPL Vacuum Tower Bttms.	Syncrude Vacuum Gas Oil	Athabasca Bitumen (220°C+)	Lloydminster Vacuum Gas Oil	Lloydminster Atmospheric Tower Bttms.
Vol.% of Crude		19.3	10.0	31.3	100	28.0	72.0
°API (ASTM D4052-81)		24.6	12.5	17.3	7.5	19.8	8.6
Specific Gravity @ 15°C		0.9065	0.9819	0.9509	1.0181	0.9345	1.0093
Aniline Pt., °C (ASTM D611)		94.8	NP	61.1	—	65.7	NP
Viscosity, cSt @ 100°C (ASTM D445)		8.291	595.2	8.068	150.92	6.570	373
Conradson Carbon Residue, wt% (ASTM D189)		0.78	19.5	0.07	13.5	0.04	17.3
Asphaltene Content, wt% (ASTM D3279)		0	6.4	0	12.4	0	14.2
Pen @ (°C) (ASTM D5)		NP	321 (25)	NP	NP	NP	>312 (0)
S, wt% (ASTM D2622)		0.49	1.06	0.438	4.91	2.34	5.27
N, wt% (ASTM D3431)		0.094	0.478	0.132	0.422	0.050	0.394
Ni, ppm (GCM 239)		<0.05	40.4	<0.05	65.1	0.04	63.1
V, ppm (GCM 239)		<0.05	22.4	<0.05	204	0.2	136
Fe, ppm (GCM 239)		—	—	—	917	0.14	35.9
Cu, ppm (GCM 239)		—	—	—	0.12	0.02	0.57
Distillation Data (GCM 379)	IBP, °C	118	286	344	248	139	337
	5%	333	470	364	308	366	376
	10%	367	557	372	349	376	401
	30%	424	609	395	485	399	500
	50%	462	—	419	624	420	612
	70%	501		446	—	445	—
	90%	555		491		488	
	95%	576		511		515	
	FBP	627		577		587	

NP = Not Possible

TABLE 1.2

Compositions of MAT Feeds

Feed:	Mass % IPL Vacuum Gas Oil	IPL Vacuum Tower Bttms.	Syncrude Vacuum Gas Oil	Athabasca Bitumen (220°C+)	Lloydminster Vacuum Gas Oil	Lloydminster Atmospheric Tower Bttms.
Hydrocarbon Type						
Paraffins	22.8	6.74	6.47	1.61	9.21	4.88
Monocycloparaffins	15.7	11.0	9.76	6.97	10.2	9.02
Condensed Cycloparaffins	24.9	24.1	30.0	20.5	26.0	17.8
Alkylbenzenes	4.84	4.02	7.11	4.03	4.11	4.16
Benzocycloparaffins	4.95	3.84	5.89	3.87	5.40	3.34
Benzodicycloparaffins	4.08	3.74	5.50	4.85	5.94	4.81
Diaromatics	9.73	8.89	15.4	11.1	15.0	10.3
Triaromatics	4.44	6.27	8.19	4.83	6.92	6.72
Tetraaromatics	1.76	5.71	3.36	14.4	3.99	4.65
Polyaromatics & Polars	5.24	15.7	5.83	14.4	5.41	12.8
Aromatic Sulphur						
2-Ring Compounds	0.62	1.68	0.64	4.34	3.75	3.61
3-Ring Compounds	0.76	0.56	1.79	2.83	3.07	2.10
4-Ring Compounds	0.18	1.31	0.04	1.95	0.66	1.60
Asphaltenes	0.	6.4	0	12.5	0	14.2
Total	100.00	100.00	100.00	100.00	100.00	100.00
Precursors						
gas + gasoline	77.3	53.4	64.7	41.8	60.9	44.1
light cycle oil	10.7	10.9	16.9	16.9	20.3	15.0
decant oil	12.0	35.8	18.4	41.3	18.8	40.9

2) CATALYST CHARACTERIZATION

Three 500 g samples of commercial equilibrium fluid catalytic cracking catalysts - Super DX, GRZ-1, and DA-300, were obtained from Davison Division of W.R. Grace for this study. Physical and compositional properties of these materials are listed in Table 2.1. Davison literature indicates that Super DX is a coke-selective catalyst meant for cracking gas oils and it is not particularly tolerant of metals in the feedstock (Ni + V). DA-300 and GRZ-1, however, are both metals-tolerant catalysts designed specifically for residuum cracking.

Microactivity determinations indicate that Super DX and DA-300 catalysts have similar cracking activities (MA = 70). The surface areas (69 and 67 m^2/g), pore volumes (0.60 and 0.57 g/cc) and apparent bulk densities (0.94 and 0.95 g/cc) of these two catalysts are also very similar. The GRZ-1 catalyst is very active, which is reflected in its high microactivity value (76.9). This catalyst has a larger surface area (98 m^2/g), greater pore volume (0.73 g/cc) and lower apparent bulk density (0.77 g/cc) than the other two less active catalysts. Directionally, these properties reflect the greater reactivity of this sample of GRZ-1 since fresher, more active catalyst has a greater surface area, greater pore volume and lower apparent bulk density than older catalyst. With use, catalyst is degraded and poisoned which tends to reduce surface area, pore volume and increase apparent bulk density.

Fluid catalytic cracking catalysts are poisoned by metals such as nickel and vanadium, which are present in gas oils and residual feeds. The Super DX sample contains only 380 ppm vanadium and 190 ppm nickel. GRZ-1 has 517 and 678 ppm vanadium and nickel, while DA-300 contains 2144 and 694 ppm vanadium and nickel. The low levels of metals on Super DX is consistent with the catalyst's intended use with gas oils which contain relatively low concentrations of nickel and vanadium species. GRZ-1 and DA-300 contain higher metals loadings, both have similar levels of nickel but GRZ-1 has far less vanadium than does DA-300. This is due to the feedstock these catalysts have been exposed to and whose nickel/vanadium ratios vary greatly. To bring all metals

contamination to a single value, Shell use the concept of a contamination index (CI) [5]:

$$CI = 1000\ (Fe + 4\ V + 14\ Ni + 14\ Cu)\ \text{all metals in ppm}$$

Since the levels of copper are low and iron is not too detrimental, this readily parallels the concept of nickel equivalents:

$$\text{Ni equivalents} = Ni + V/4$$

With these relationships, all metals contamination can be lumped, but it is misleading because nickel and vanadium affect the catalyst by different mechanisms.

Residual carbon contents on the catalysts were also determined since they affect catalyst activity and are required to calculate the net carbon yield during the microactivity tests. Both Super DX and DA-300 have residual carbon contents of 0.14 and 0.15 wt.%, respectively, while GRZ-1 has a slightly higher level of 0.23 wt.%. None of these materials has sufficiently high residual carbon contents so as to reduce its activity.

Physical properties of the catalysts, such as particle size distribution, cumulative pore size distribution and appearance by scanning electron microscopy, are shown in Table 2.1, Figure 2.1 and Figure 2.2 respectively. These catalysts are essentially smooth, spherical solids of uniform size. When cleaved, these spherical solids can be seen to be composed of agglomerates of much smaller particles which include both active zeolites and relatively inactive binder. As a result, the spherical catalyst particles are very porous, allowing for rapid diffusion of high molecular weight hydrocarbons into them.

TABLE 2.1

Physical and Compositional Properties of Catalysts

Catalyst	Super DX	GRZ-1	DA-300
Identification No.	CKM 80	SMR5-2601 Item 1	SMR5-2601 Item 2
Microactivity (% Con.)	70	76.9	70.1
Surface Area (M^2/g)	69	88	67
Pore Volume (cc/g), Hg	0.60	0.73	0.57
Apparent Bulk Density, g/cc	0.94	0.77	0.95
Elemental Analysis			
V, ppm	380	950	2744
Ni, ppm	190	678	694
Cu, ppm	50	—	—
Na, wt%	0.38	0.75	0.38
Fe, wt%	0.46	1.08	0.59
C, wt%	0.14	0.23	0.15
Al_2O_3, wt%	31.5	25.0	40.8
Particle Size, wt%			
0-20 microns	2	0	3
0-40 microns	13	2	21
0-80 microns	75	72	64
APS	63	69	66

FIGURE 2.1

Cumulative Pore Size Distribution of Catalysts

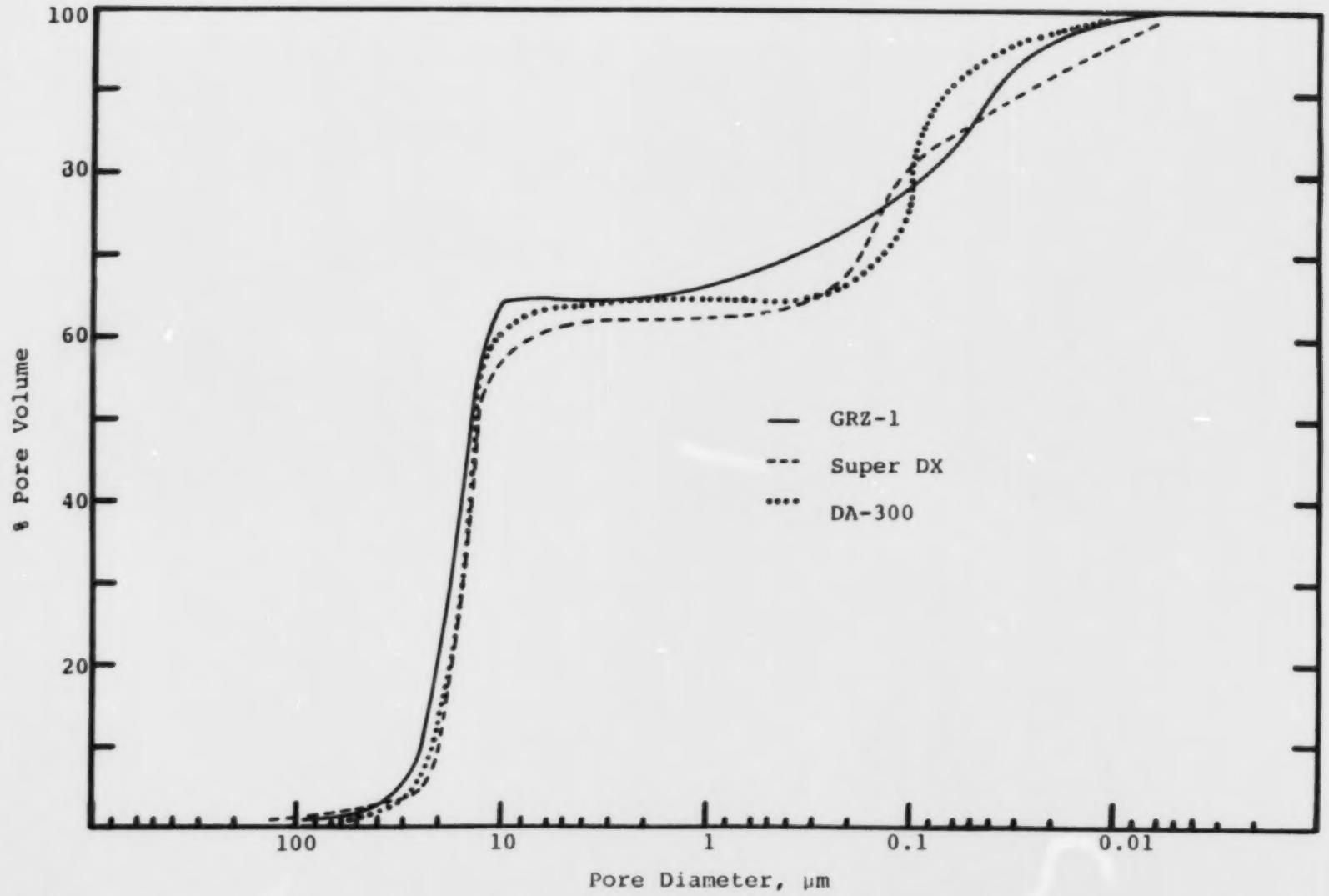


FIGURE 2.2

SEM MICROGRAPHS OF DA-300 RESID CRACKING CATALYST

Magnifications

3) EXPERIMENTAL DESIGN

The microactivity test apparatus mimics a commercial FCCU in some but not all operating features. The obvious difference is that the former uses a fixed bed while the latter employs an entrained bed. The MAT also only cracks feedstock in a batch contact to produce a spent catalyst, where the commercial unit both cracks feedstocks and regenerates catalyst to give a thermally balanced continuous operation. For the commercial units the independent operating variables are: reactor temperature, combined feed rate, feed preheat temperature, reactor pressure and catalyst activity. This results in the regenerator temperature, conversion and catalyst to oil ratio (C/O) becoming dependent variables [6]. With the microactivity test apparatus, cracking temperatures are maintained by the application of heat by furnaces and the C/O ratio can be adjusted at will. This implies that for the MAT both temperature and C/O are independent variables while the conversion remains a dependent variable. The MAT, therefore, allows a wider range of operating conditions to be evaluated as do most FCC pilot plants [7] which are also not thermally balanced.

For this study both reactor temperature and C/O ratio have been treated as independent variables. For each combination of catalyst and feedstock, at least nine MAT tests in a full 3x3 factorial design experiment were carried out at three C/O ratios and three temperatures. The product yields determined covered a range of conversions which included typical commercial operations.

Data from the factorial designed experiments showed that conversions of feed (100-LCO-DO) had a strong dependence on C/O ratio with a smaller effect due to temperature also being noted. Coke yield appeared to be linearly proportional to C/O ratio and dependent on temperature. All other product yields seemed largely dependent on conversion, although some temperature effects were noted. The data for conversion versus C/O, coke yield versus C/O and other products versus conversion were displayed graphically so that these correlations could be used to estimate MAT data for any desired conversion or coke yield within the range of conditions studied.

This will prove particularly useful in comparing both feeds and catalysts since yields at comparable conditions can be estimated and individual yields can be smoothed.

Since the experiments performed for each catalyst or feedstock evaluation were of a factorial design, attempts were made to statistically fit conversion and product yield data to quadratic functions of the independent variables, reactor temperature and C/O ratio. The purpose of this was to obtain even better estimations of yields and determine whether or not the correlations could produce meaningful trends when compared. Conversion and coke yield were found to correlate well with reactor temperature and C/O ratio, while other product yields fitted best with reactor temperature and conversion.

4) MAT PRODUCT DATA FOR CATALYSTS AND IPL VGO

IPL VGO, a common Canadian FCCU feedstock, was used to evaluate the three catalysts chosen for this study. Results of MAT experiments with IPL VGO and Super DX, GRZ-1 and DA-300 were used to form the basis for selection of the catalyst with which to proceed with resid cracking studies.

MAT product yields for IPL VGO and Super DX are listed in Table 4.1. For this combination of catalyst and feedstock the relationships between conversion and C/O ratio, coke and C/O ratio, and product yields and conversion are presented graphically in Figures 4.1, 4.2, and 4.3, respectively. These results show that conversion increases 5.3 mass % for each unit increase in C/O ratio over a C/O range of 4 to 7 and a reactor temperature range of 425 to 475°C. Also, for each 25°C increase in temperature at given C/O, conversion increases between 0.75 and 3 wt.%. This illustrates the effect of both temperature and C/O ratio on cracking severity and therefore on conversion.

The coke selectivity of the catalyst can be evaluated by considering the relationship between C/O and coke. Data in Figure 4.2 show the IPL/VGO relationship is linear but

temperature dependent:

coke yield (wt.%) = 1.046 (C/O) - 0.368 T = 425
coke yield (wt.%) = 0.9892 (C/O) - 0.613 T = 450
coke yield (wt.%) = 0.9091 (C/O) - 0.773 T = 475

This results in lower coke yield at a given C/O with increased temperature, which seems contrary. Note we have neglected some data points at high C/O ratios and lower temperatures because as C/O ratio increases, a point is reached where coke yield fails to increase appreciably due to lack of precursors. These data appear to fail in such a regime.

Product yields for IPL VGO and Super DX (Figure 4.3) indicate the C_6+ gasoline maximum (48.1 wt.%) occurs at 76% conversion. At higher conversions, the yield of light ends and C_3 C_4s increased dramatically as does coke yield. Light cycle oil and decant oil decrease with conversion and for conversions >76% gasoline yield also decreases dramatically. At these higher conversions gasoline is being converted to light ends faster than cycle oils are being converted to gasoline or other products, as can be seen from the selectivity (C_6+ gasoline/Conversion, Figure 4.4). These yields are typical of those found by others [8]. Product yields were also fit to operating variables such as T, C/O ratio and conversion (Table 4.2).

IPL VGO MAT experimental results with GRZ-1 and DA-300 can be found in Tables 4.3 and 4.5, respectively. For these combinations of feedstocks and catalysts, the relationships between conversion and C/O ratio (Figures 4.5 and 4.9), coke and C/O ratio (Figures 4.6 and 4.10), product yield and conversion (Figures 4.7 and 4.11) and hydrogen, gasoline and coke selectivities (Figures 4.8 and 4.12) are also presented graphically. For GRZ-1 the response of conversion to C/O ratio is very high (7.5 wt.% per unit increase of C/O) at low C/O ratios consistent with the catalyst's activity. The conversion appears to approach a maximum asymptotically at successively lower conversions as temperature is decreased. The high level of these maxima (80-83 wt.%) suggests most of the precursors in the feedstocks have been depleted. The effect of temperature on conversion with GRZ-1 is slightly less than that experienced with Super DX and is 5 wt.% for each 40°C increase in temperature. This comparison is not

completely valid since the temperature ranges are different. With DA-300 the effect of C/O on conversion is similar to that of Super DX. Conversions were lower (60-80 wt.%) and did not approach an asymptotic maxima. Temperature increased DA-300 conversions of IPL VGO by at most 5 wt.% for a 40°C increase in reaction temperature.

Coke selectivity for both GRZ-1 and DA-300 can also be evaluated graphically from their coke-C/O relationships. For GRZ-1 and IPL VGO these relationships are linear:

$$\text{coke} = 1.309\ (C/O) + 0.38 \qquad T = 450$$
$$\text{coke} = 1.634\ (C/O) - 1.11 \qquad T = 470$$
$$\text{coke} = 1.849\ (C/O) - 1.44 \qquad T = 490$$

DA-300 and IPL VGO gave the following linear dependencies of coke on C/O

$$\text{coke} = 1.043\ (C/O) + 0.59 \qquad T = 450$$
$$\text{coke} = 1.330\ (C/O) - 1.11 \qquad T = 470$$
$$\text{coke} = 1.121\ (C/O) - 0.354 \qquad T = 490$$

With GRZ-1, coke yield increases with temperature while with DA-300 maximum coke yield occurs at an intermediate temperature. Comparing the slopes of these equations for the different catalysts at 450°C and 470/475°C shows that Super DX is the most coke selective catalyst, followed by DA-300 and GRZ-1 respectivley. At 450°C Super DX and DA-300 have very similar coke selectivities (0.9892 vs 1.043) while at 470/475°C Super DX is much more selective (0.909 vs 1.330) in spite of both catalysts having the same microactivity. The very poor coke selectivity of GRZ-1 can be attributed to its very high activity, which leads to both high conversions and large coke yields.

Product yields for GRZ-1 and DA-300 as a function of conversion are also quite different. With GRZ-1 as with Super DX all product yields, other than coke, vary uniformly with conversion and temperature effects are not appreciable. With DA-300, however, distinct temperature effects on light ends, C_3 C_4 and C_6+ gasoline product yields are noted.

Increasing reactor temperature increases light ends and C_3 C_4 yields while lower temperatures favoured gasoline formation. GRZ-1 produced a maximum gasoline yield of 42% at 73-75% conversion and C_6+ yield fall off quickly with conversion, while DA-300 gives a shallow 45.5 wt.% maximum gasoline at 450°C and 43 wt.% maximum gasoline at 490°C at 72-73% conversion. These both compare unfavourably to Super DX, which yielded 48.1 wt.% C_6+ gasoline at 76% conversion for IPL VGO. At conversions greater than that necessary for maximum gasoline yield, coke make increased very rapidly for GRZ-1 and less rapidly for Super DX and DA-300. Total liquid yields at maximum gasoline yield (C_3 C_4, C_6+ & LCO) are 71, 72.5, 76.5% for indicating DA-300 is superior catalyst.

Statistical analyses of data (Tables 4.2, 4.4 and 4.6) indicate that coke yield and conversion can be fit to simple functions of temperature and C/O while other yield data can be fit to similar simple functions of temperature and conversion. The root mean square error for coke yield is very low (0.25-0.50%) and well within the experimental error expected. Other conversion and yield correlations are fit to approximately that of the experimental error which gives reasonable confidence in the fit.

Super DX is not a resid cracking catalyst but development of its yield structures was necessary to compare conventional FCCU catalyst with resid cracking catalysts. For the samples of resid cracking catalysts obtained, DA-300 appeared superior to GRZ-1 because 1) it has greater metals loading, 2) it is more coke selective, 3) it gives greater gasoline yields, and 4) it gives greater yields of total liquid products. GRZ-1 at comparable activity may well be a suitable catalyst but for this work it was judged far too active.

TABLE 4.1

MAT Product Yield Data for IPL Vacuum Gas Oil and Davison Super DX

st	MAT 302	MAT 303	MAT 304	MAT 274	MAT 273	MAT 207	MAT 208	MAT 275	MAT 276	MAT 277
s Balance, wt%	99.4	97.8	98.9	99.3	99.9	101.6	101.4	99.4	99.8	100.7
°C	425	425	424	450	450	450	450	476	474	475
), g/g	2.80	4.36	7.08	2.87	4.61	6.96	6.95	3.13	4.95	7.05
elds, wt% FF										
H_2	0.02	0.03	0.02	0.03	0.04	0.05	0.06	0.03	0.04	0.09
CH_4	0.08	0.14	0.32	0.16	0.23	0.46	0.55	0.26	0.39	0.97
C_2	0.53	0.90	1.45	0.64	1.04	1.79	2.00	1.02	1.43	2.98
C_3	1.83	3.35	4.84	3.61	4.28	4.85	5.27	4.38	5.30	7.88
C_4	3.80	6.77	9.45	7.58	9.07	8.63	8.84	8.76	10.6	14.4
C_5	3.53	4.48	6.25	4.44	4.58	7.71	7.80	4.39	5.98	8.23
C_5+ gasoline	35.6	47.4	53.2	43.4	47.9	55.9	55.3	44.0	49.9	48.4
C_6+ gasoline	32.0	42.9	47.0	39.0	43.3	48.2	47.5	39.6	44.0	40.2
LCO	24.2	23.2	17.9	22.8	20.6	17.7	16.7	20.7	17.8	13.2
DO	31.5	14.3	8.39	19.6	13.5	6.69	7.32	19.1	11.2	7.53
Coke	2.54	4.18	4.70	2.37	3.71	4.48	4.55	2.02	3.79	5.61
nversion	44.3	62.6	73.7	57.6	66.0	75.7	76.0	60.2	71.0	79.3
+ gasoline/Conversion	0.722	0.685	0.638	0.677	0.656	0.637	0.625	0.658	0.620	0.507
ke/Conversion	0.0573	0.0668	0.0638	0.0411	0.0562	0.0591	0.0599	0.0336	0.0534	0.0707
+ gasoline/coke	12.6	10.3	10.0	16.5	11.7	10.8	10.4	19.6	11.6	7.17

FIGURE 4.1
The Effect of C/O Ratio on Conversion for IPL VGO and Super DX

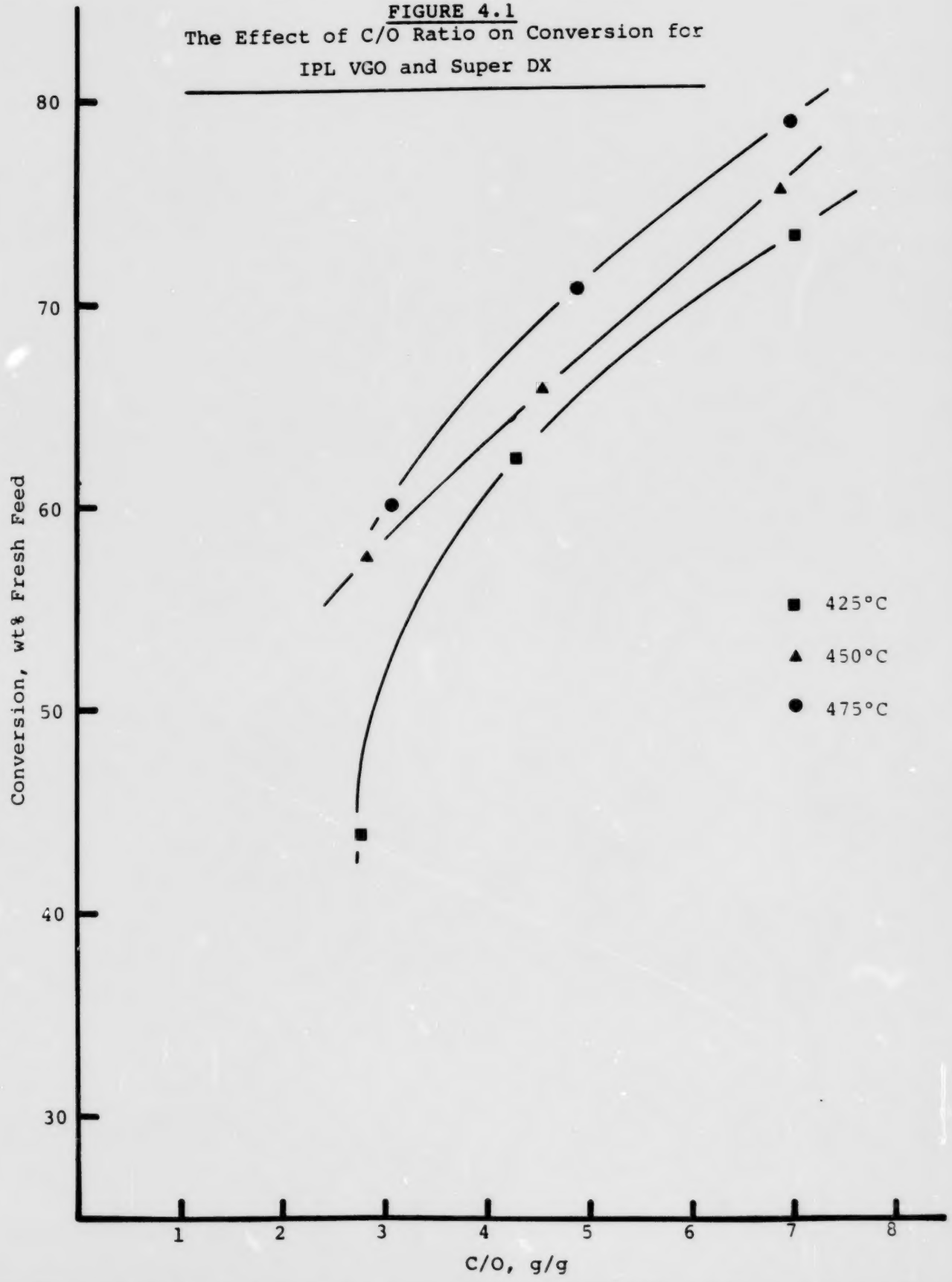


FIGURE 4.2

The Dependence of Coke Yield on C/O Ratio for IPL VGO and Super DX

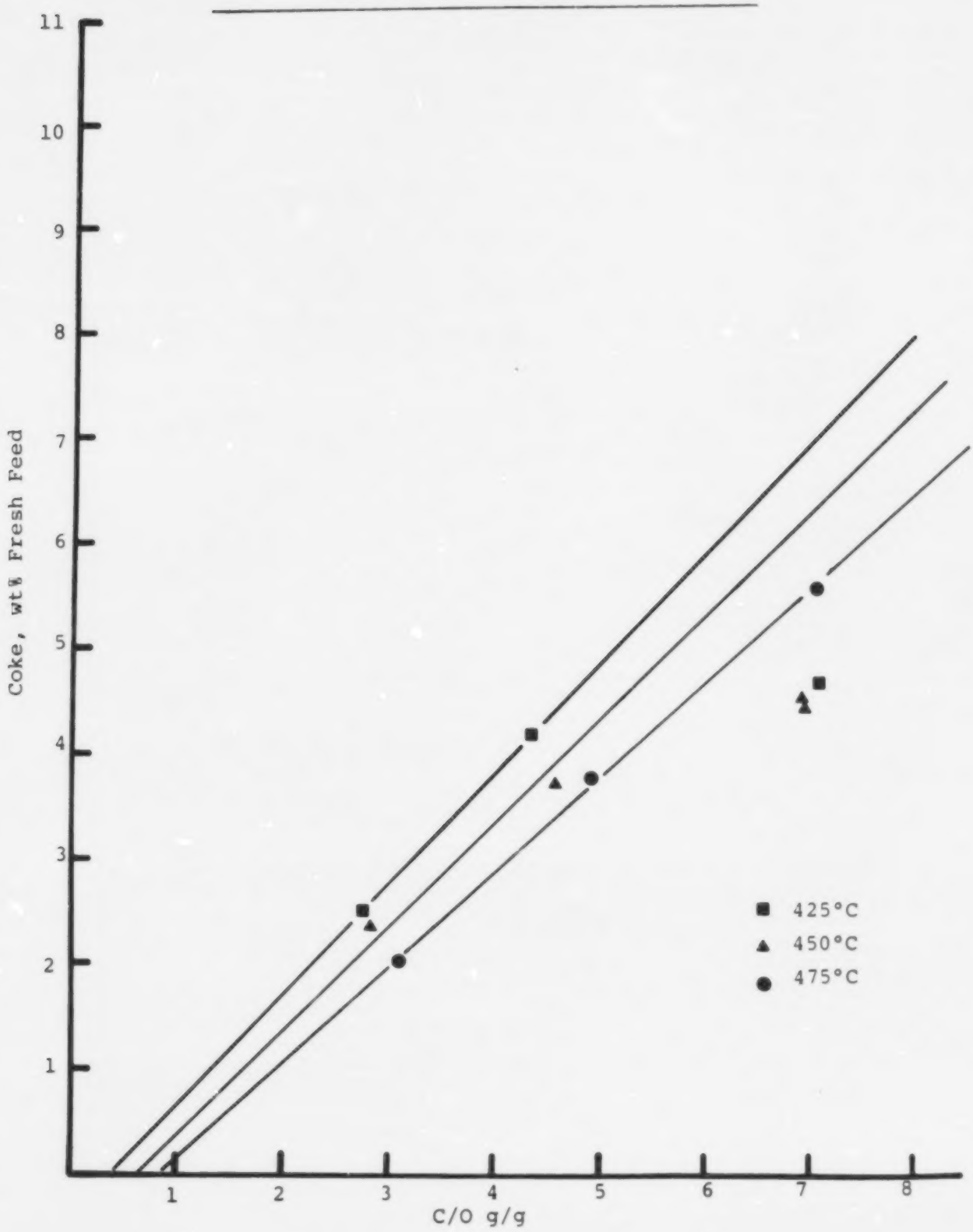


FIGURE 4.3

The Effect of Conversion on MAT Product Yields of IPL VGO with Super DX

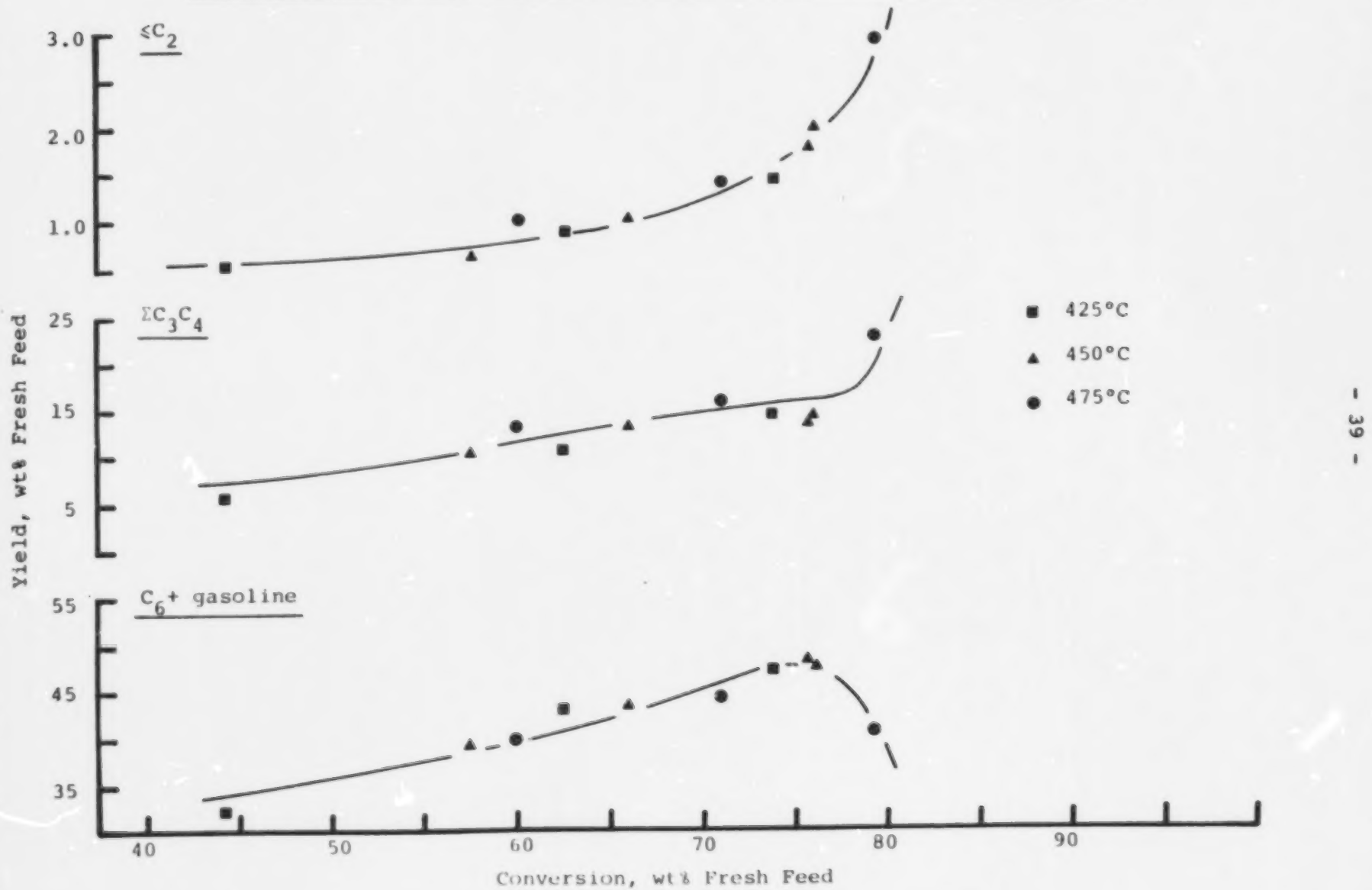


FIGURE 4.3 (continued)

The Effect of Conversion on MAT Product Yields of IPL VGO with Super DX
(Continued)

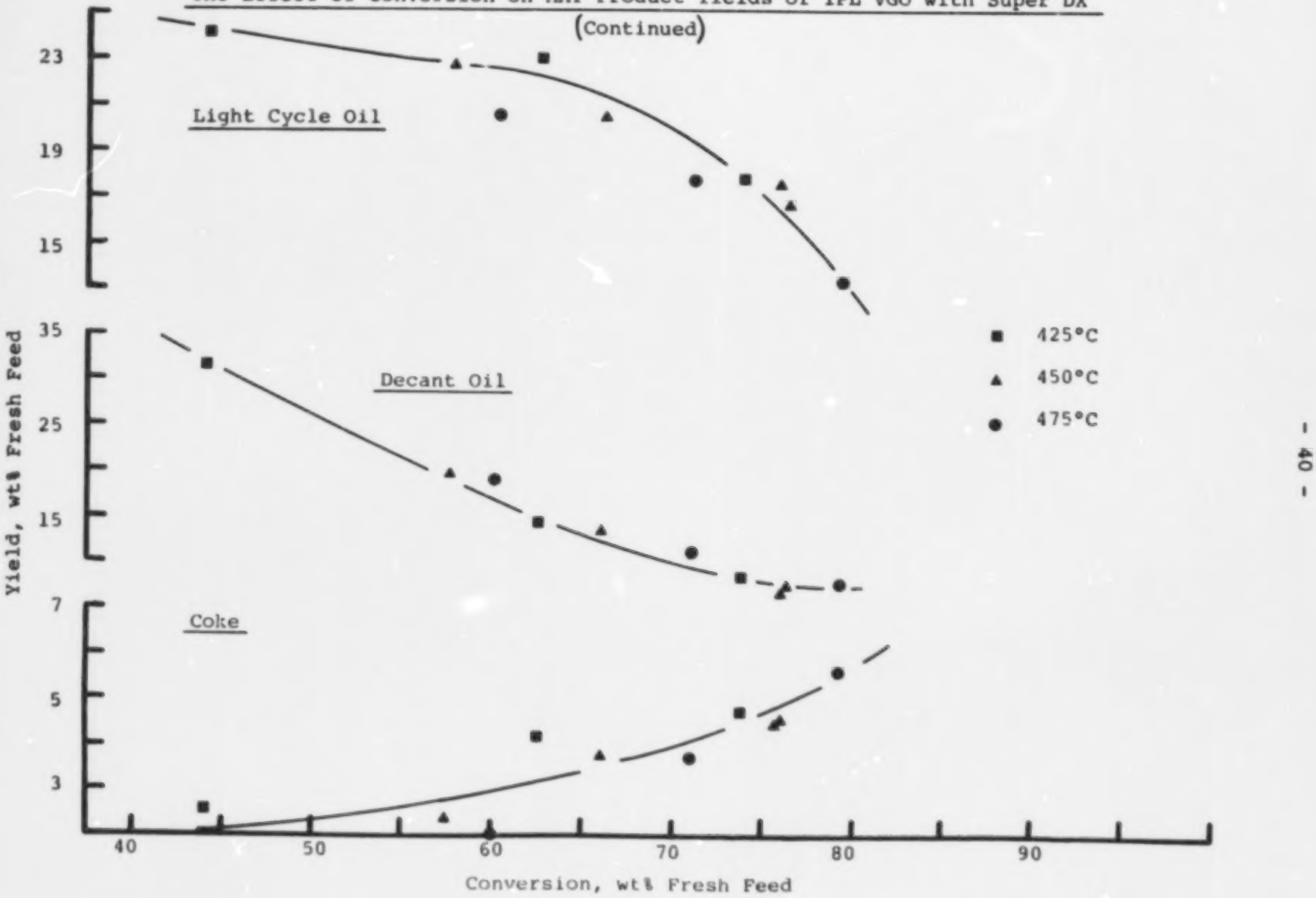


FIGURE 4.4

The Effect of Conversion on MAT Product Ratios of IPL VGO with Super DX

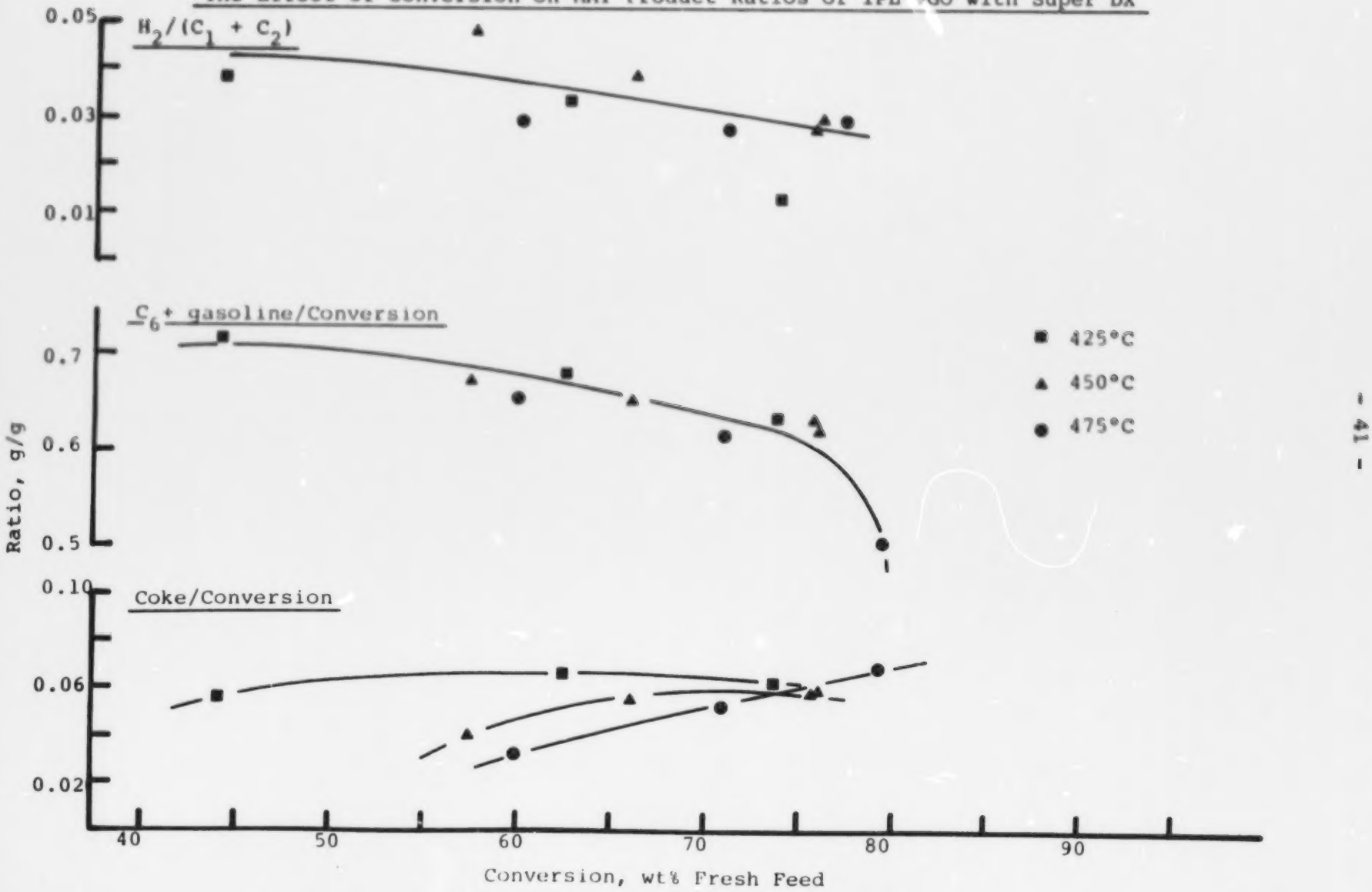


TABLE 4.2

Summary of Regression Analyses for IPL VGO and Super DX

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE %
H_2	0.6932		-0.02374	-5.6189E-05	3.7411E-06		0.8649	0.0096
ΣC_2	7.4218		-0.3211	0.0001294		0.002523	0.9462	0.2089
ΣC_3	-5.9703				3.2516E-05	0.0008659	0.9042	0.5507
ΣC_4	-2.6765		-0.2286	0.0008885			0.8469	1.1993
ΣC_5	15.8419		-0.5035			0.005161	0.9547	0.4102
C_6+ gaso.	-220.7210	0.5343	4.4328	-0.009073			0.8957	1.9411
LCO	43.0688			0.003223	-0.0002939	-0.01339	0.9763	0.6183
DO	89.9939		-1.9568		5.0890E-05	0.009682	0.9962	0.5897

Coke Yield (wt.%) = 0.820 + 0.586 (C/O) — R^2 = 0.8414, Root MSE % = 0.49

Conversion (wt.%) = $-49.56 + 13.90\ (C/O) + 0.1157(T) - 0.8507\ (C/O)^2$ — R^2 = 0.9558, Root MSE % = 2.76

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

TABLE 4.3

MAT Product Yield Data for IPL Vacuum Gas Oil and Davison GRZ-1

Test	MAT 314	MAT 315	MAT 318	MAT 319	MAT 321	MAT 320	MAT 322	MAT 323	MAT 324
Mass Balance, wt%	101.1	101.8	103.3	101.7	102.5	103.0	100.3	102.4	102.6
T, °C	450	451	450	470	470	468	490	490	489
C/O, g/g	2.75	4.60	7.04	2.76	4.97	6.36	2.63	4.54	6.67
Yields, wt% FF									
H_2	0.06	0.11	0.17	0.06	0.14	0.22	0.09	0.16	0.30
CH_4	0.19	0.39	0.74	0.27	0.65	1.21	0.50	0.97	2.09
ΣC_2	1.03	1.82	2.95	1.23	2.44	3.99	1.80	3.11	5.57
ΣC_3	3.77	5.56	7.3	4.15	6.57	8.37	5.50	7.48	9.90
ΣC_4	8.03	12.0	14.9	8.47	13.4	15.9	10.2	13.9	17.2
ΣC_5	4.22	6.82	9.24	4.92	8.17	9.29	5.28	7.45	9.92
C_5+ gasoline	45.2	48.8	45.7	44.7	48.4	44.1	44.3	46.0	41.3
C_6+ gasoline	40.9	42.0	36.5	39.8	40.2	34.8	39.0	38.5	31.3
LCO	17.2	13.7	11.5	15.7	12.6	10.4	13.9	11.9	9.85
DO	20.8	11.4	7.86	22.2	9.62	7.86	20.7	10.8	5.06
Coke	3.99	6.63	9.70	3.55	6.91	9.42	3.54	6.87	11.1
Conversion	62.0	74.9	80.6	62.1	77.7	81.7	65.4	77.4	85.1
C_6+ gasoline/Conversion	0.660	0.561	0.453	0.641	0.517	0.426	0.596	0.503	0.368
Coke/Conversion	0.0643	0.0885	0.120	0.0571	0.0889	0.115	0.0541	0.0887	0.130
C_6+ gasoline/coke	10.3	6.34	3.78	11.2	5.81	3.70	11.0	5.67	2.83

FIGURE 4.5

The Effect of C/O Ratio on Conversion for IPL VGO and GR2-1

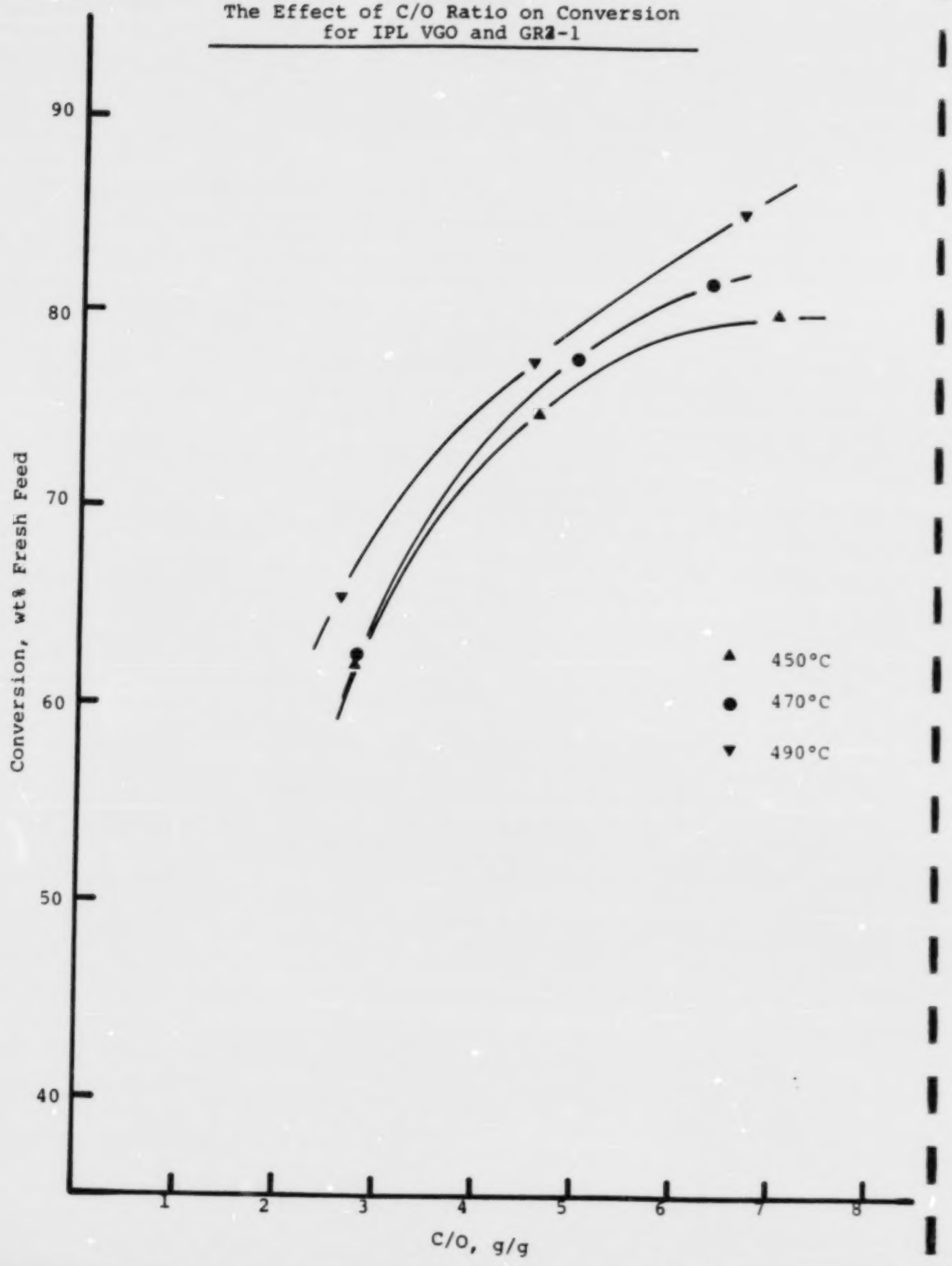


FIGURE 4.6

The Dependence of Coke Yield on C/O Ratio for IPL VGO and GRZ-1

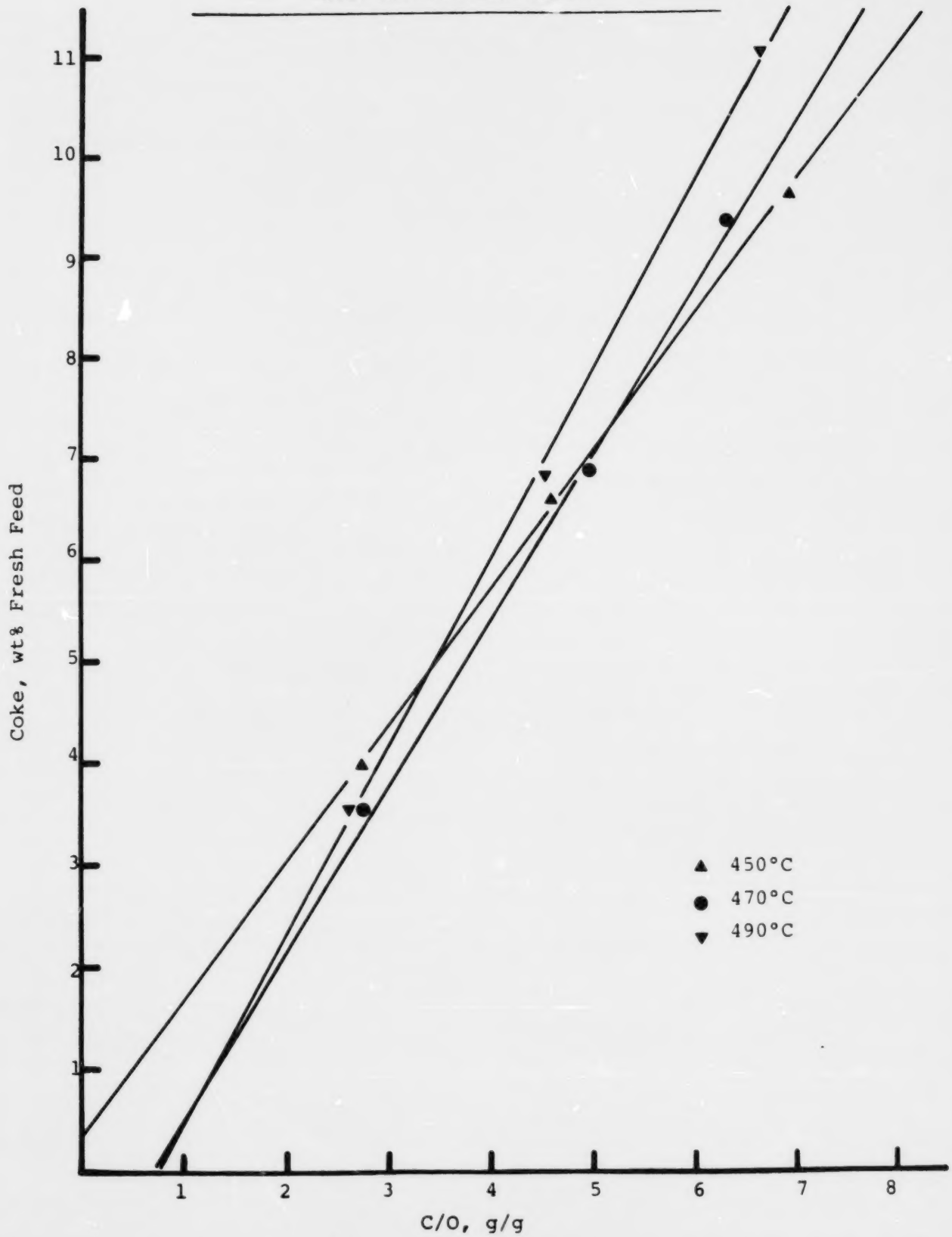


FIGURE 4.7

The Effect of Conversion on MAT Product Yields of IPL VGO with GRZ-1

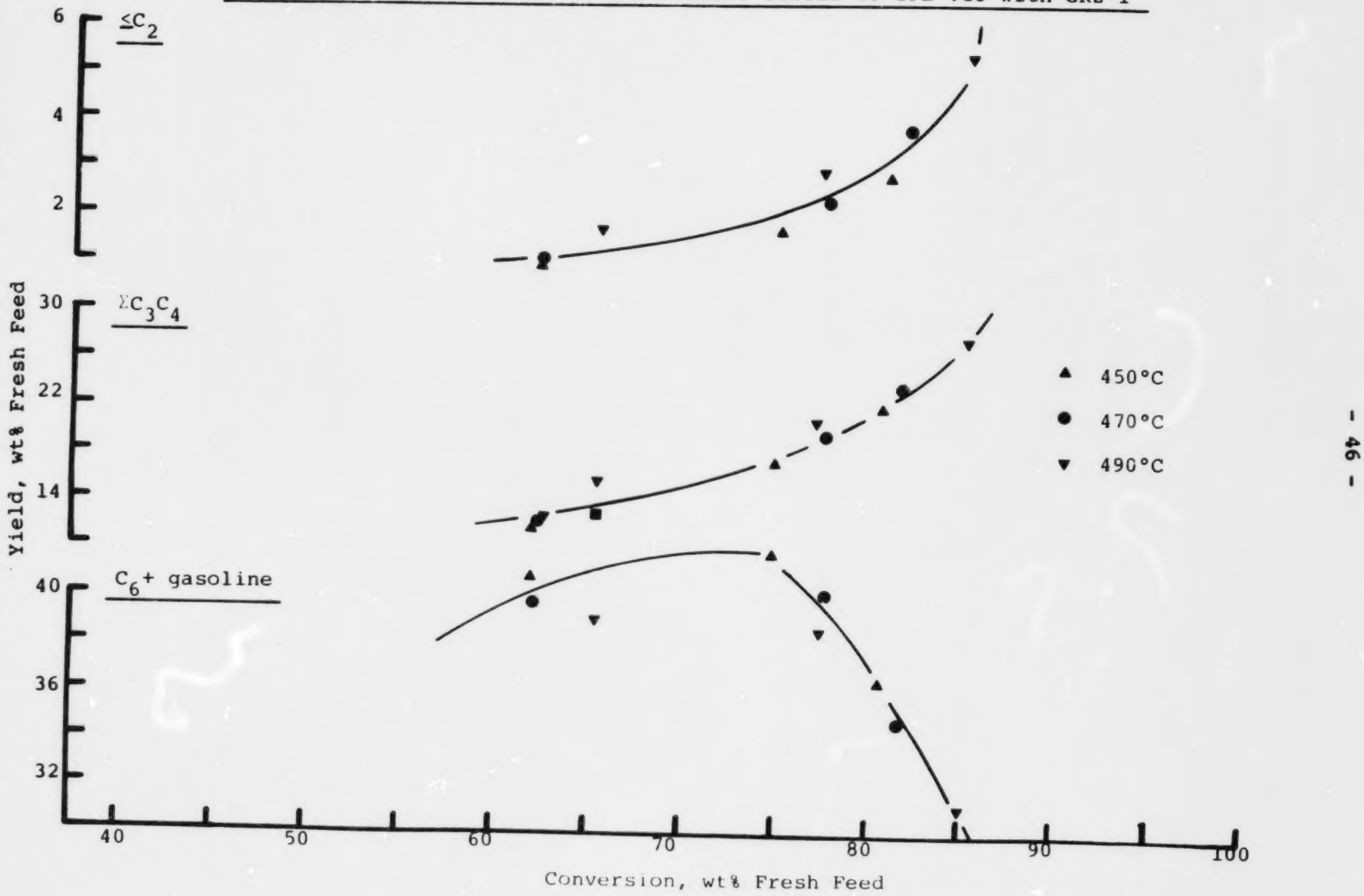


FIGURE 4.7 (continued)

The Effect of Conversion on MAT Product Yields of IPL VGO with GRZ-1

(Continued)

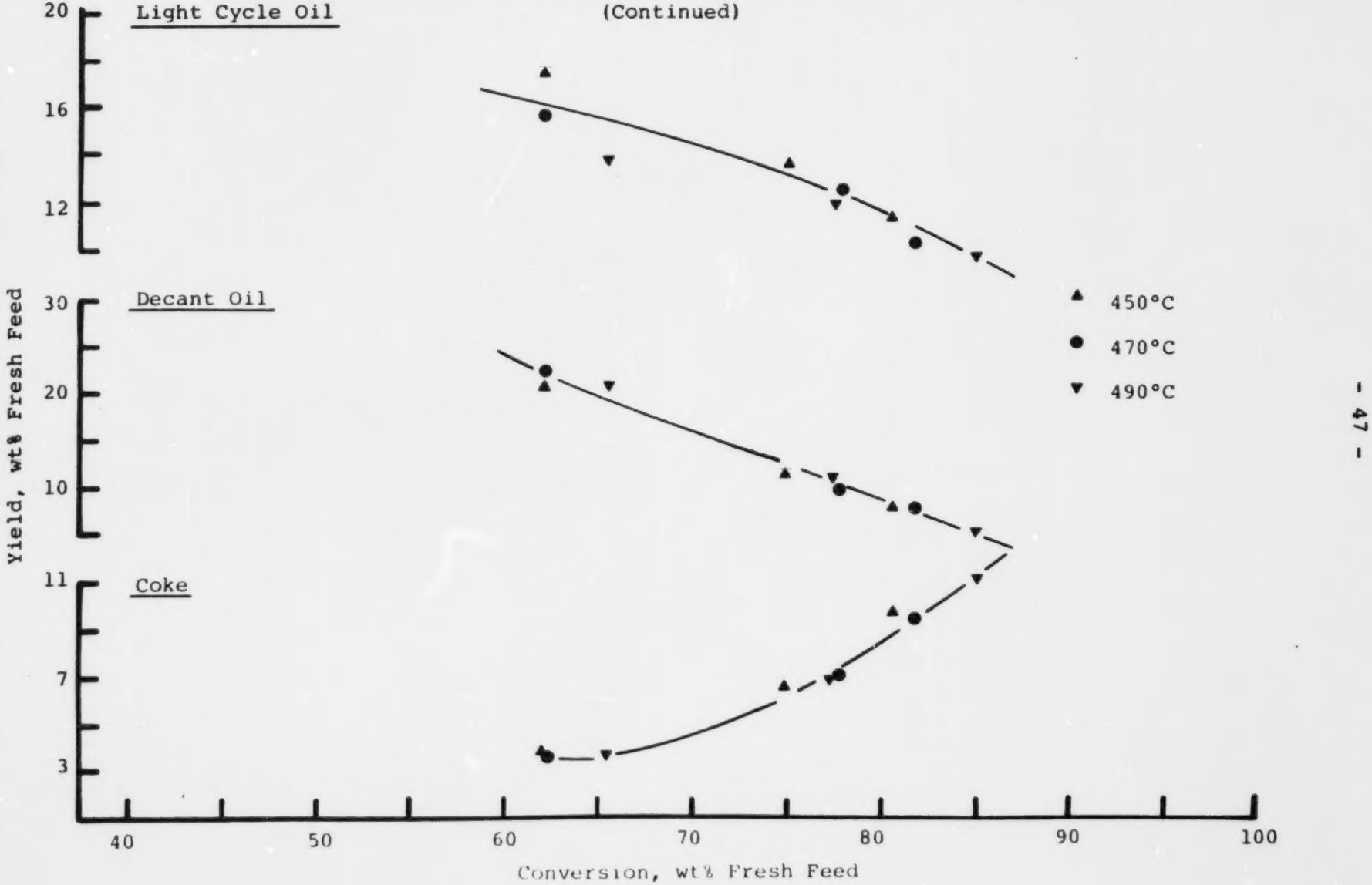


FIGURE 4.8

The Effect of Conversion on MAT Product Ratios of IPL VGO with GRZ-1

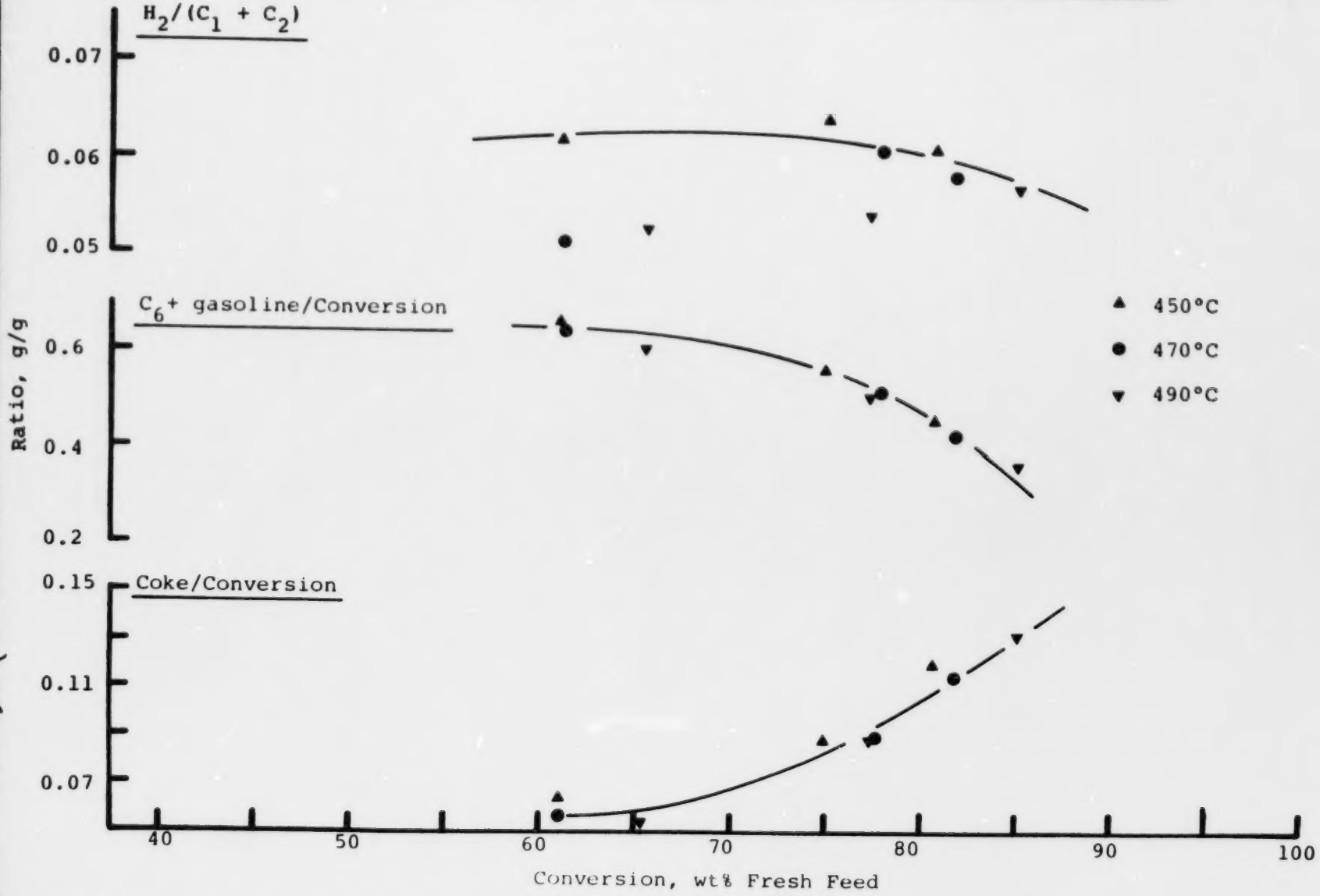


TABLE 4.4

Summary of Regression Analyses for IPL VGO and GRZ-1

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE %
H_2	2.0137	0.00083	-0.0717			0.00055	0.9889	0.01
ΣC_2	36.219	0.0227	-1.356			0.1052	0.9892	0.19
ΣC_3	15.103	0.0316	-0.8734			0.00742	0.9890	0.26
ΣC_4	4.733	0.0196	-0.4206			0.00538	0.9914	0.38
ΣC_5	-10.093		0.2341				0.9631	0.43
C_6+ gaso.	-137.000	-0.0486	5.8057			-0.04178	0.9369	1.07
LCO	137.47	-0.2254	-1.463	0.0026			0.9761	0.47
DO	51.656	0.0359	-0.7502				0.9940	0.58

Coke Yield (wt.%) = 21.3 - 4.852 (C/O) - 0.04684 (T) + 0.01376 (C/O)(T) — 0.26

Conversion (wt.%) = $-15.28 + 13.72$ (C/O) + 0.1025 (T) - 0.939 $(C/O)^2$ — R^2 = 0.9926 — 0.95

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

TABLE 4.5

MAT Product Yield Data for IPL Vacuum Gas Oil and Davison DA-300

Test	MAT 305	MAT 306	MAT 307	MAT 308	MAT 309	MAT 310	MAT 311	MAT 312	MAT 313
Mass Balance, wt%	99.4	101.3	102.7	98.2	100.8	104.7	102.2	100.7	103.0
T, °C	450	449	448	471	470	470	491	491	491
C/O, g/g	2.84	5.19	6.83	2.82	4.86	6.85	2.74	4.88	7.07
Yields, wt% FF									
H_2	0.24	0.28	0.38	0.20	0.29	0.43	0.21	0.32	0.42
CH_4	0.17	0.31	0.54	0.27	0.48	0.74	0.33	0.78	1.27
ΣC_2	1.12	1.66	2.35	1.32	2.02	2.81	1.38	2.74	3.96
ΣC_3	3.04	4.57	5.75	3.55	5.16	5.86	3.44	6.16	7.96
ΣC_4	6.47	8.78	11.7	7.10	9.63	11.6	6.38	11.3	13.8
ΣC_5	4.34	5.69	7.59	4.84	6.18	7.68	4.07	6.91	10.3
C_5+ gasoline	44.4	50.9	50.9	44.8	49.6	48.7	45.9	49.8	48.2
C_6+ gasoline	40.1	45.2	43.3	39.9	43.4	41.0	41.8	42.8	38.0
LCO	24.0	19.0	14.8	21.1	17.9	14.4	21.2	16.4	12.2
DO	17.3	9.30	6.68	19.3	10.4	8.51	19.0	8.55	6.26
Coke	3.66	5.82	7.81	2.85	5.26	8.11	2.74	5.13	7.57
Conversion	58.7	71.7	78.6	59.6	71.7	77.1	59.8	75.1	81.6
C_6+ gasoline/Conversion	0.683	0.630	0.551	0.669	0.605	0.532	0.699	0.570	0.466
Coke/Conversion	0.0624	0.0812	0.0994	0.0478	0.0733	0.105	0.0458	0.0683	0.0928
C_6+ gasoline/coke	10.9	7.76	5.54	14.0	8.25	5.06	15.3	8.34	5.02

FIGURE 4.9

The Effect of C/O Ratio on Conversion for IPL VGO and DA-300

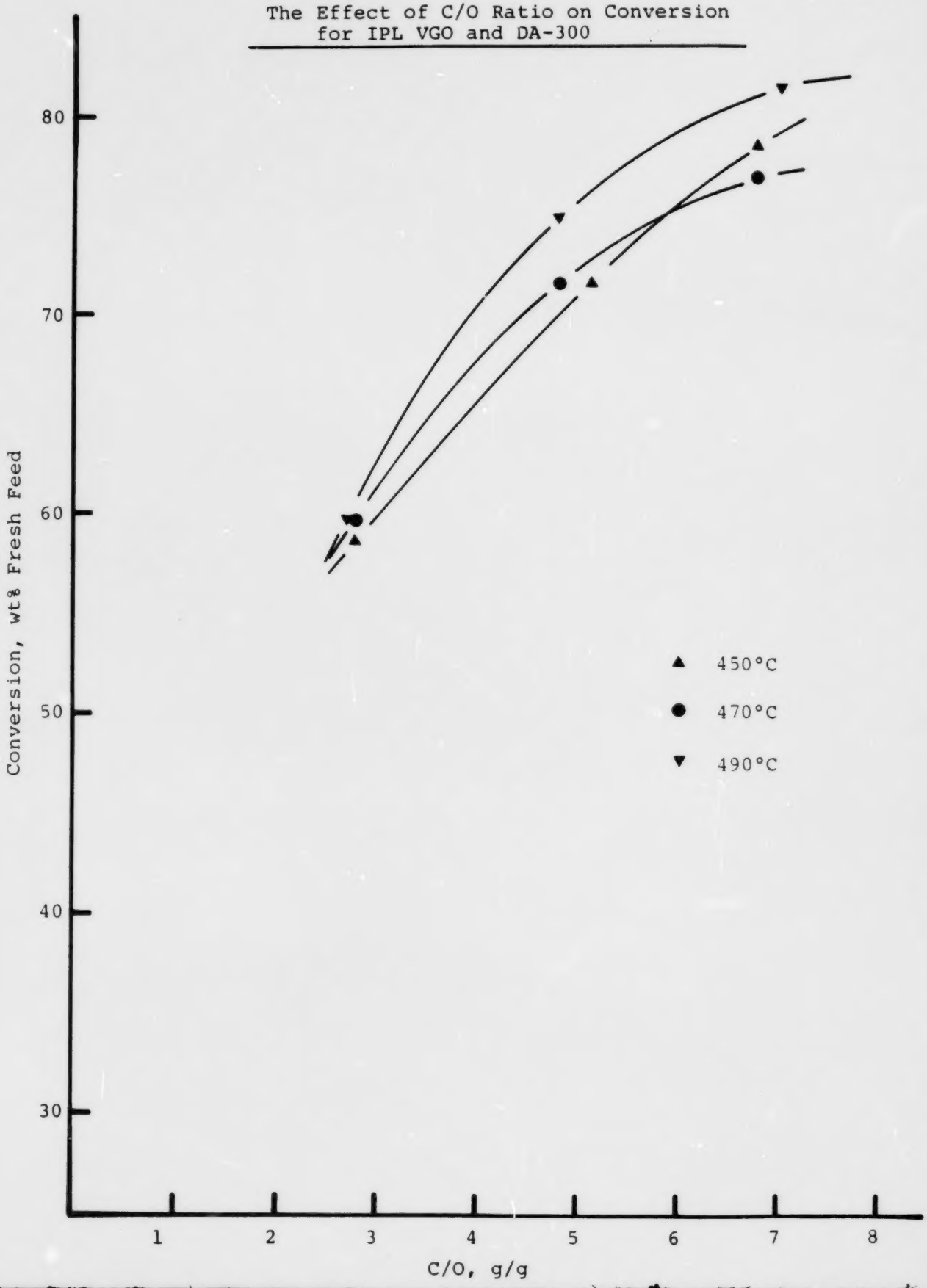


FIGURE 4.10
The Dependence of Coke Yield on C/O Ratio
for IPL VGO and DA-300

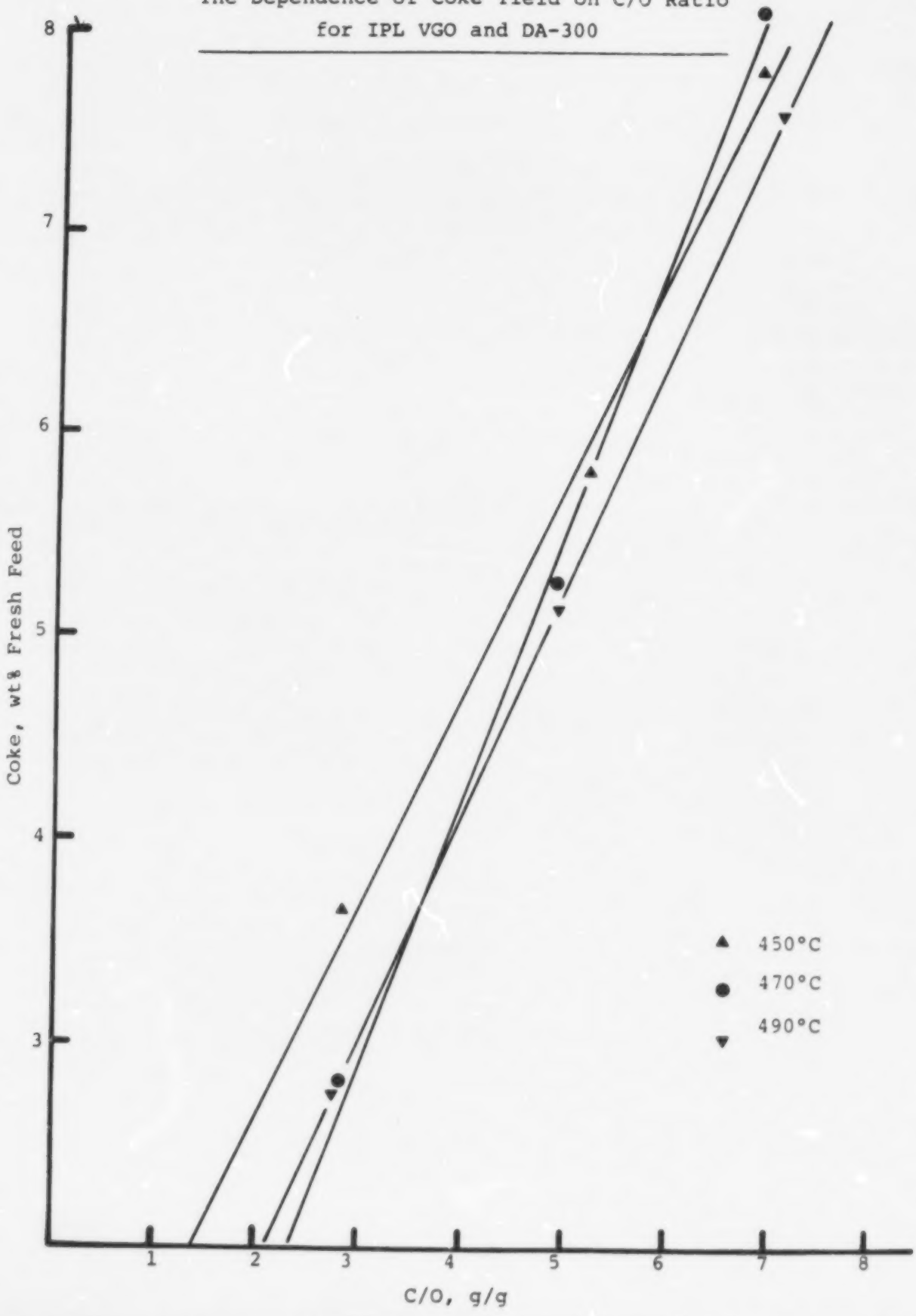


FIGURE 4.11

The Effect of Conversion on MAT Product Yields of IPL VGO with DA-300

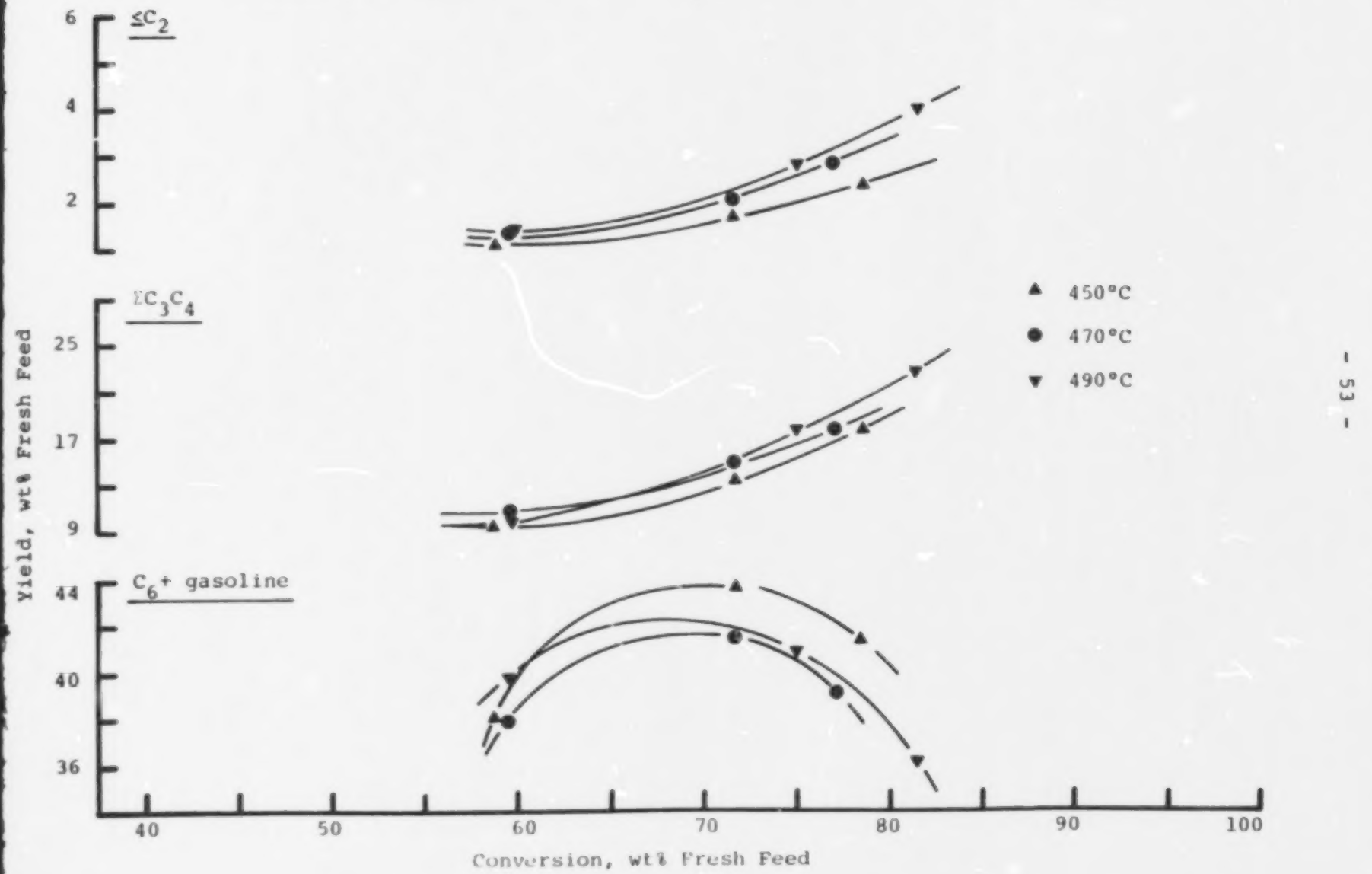


FIGURE 4.11 (continued)

The Effect of Conversion on MAT Product Yields of IPL VGO and DA-300 (Continued)

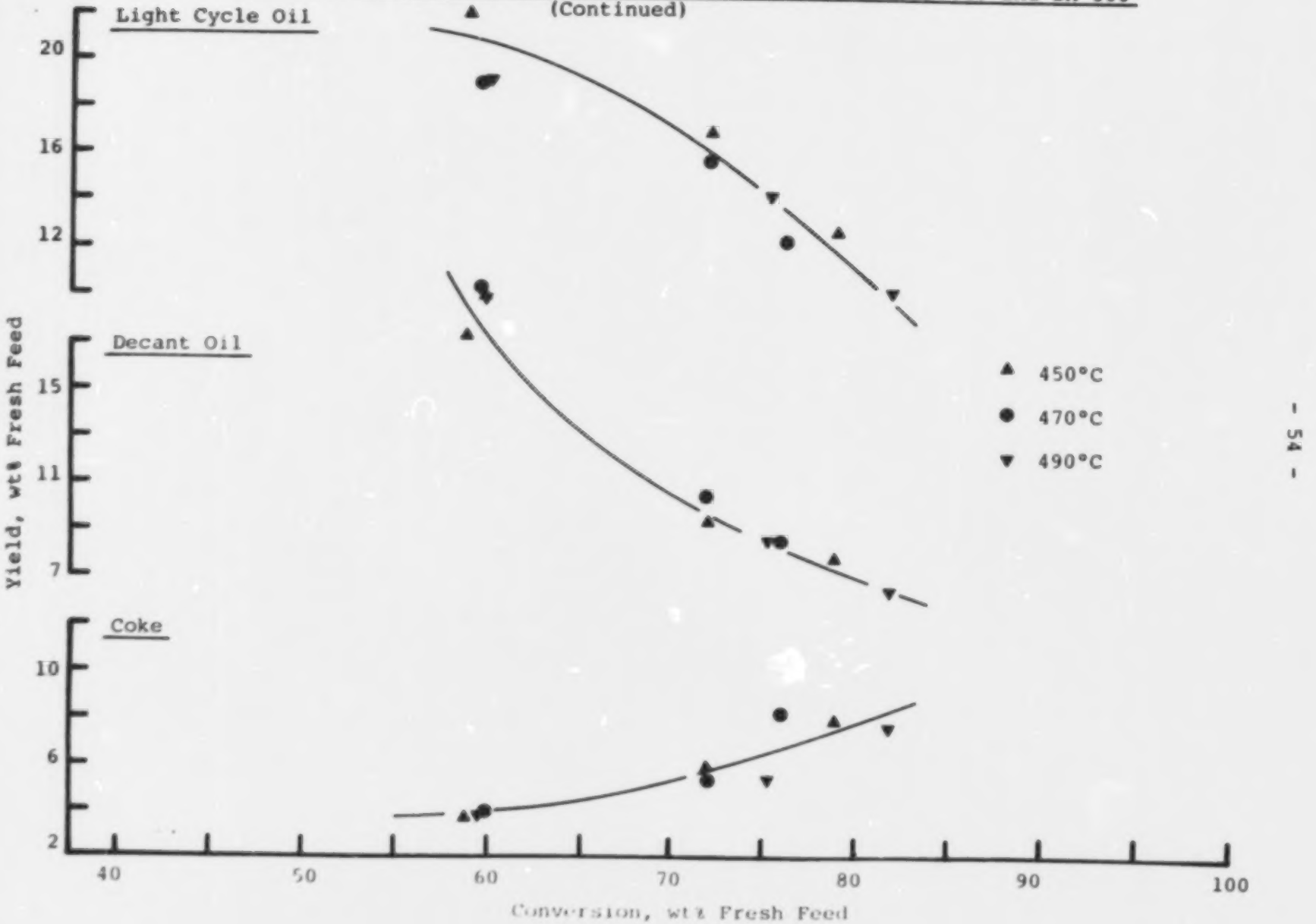


FIGURE 4.12

The Effect of Conversion on MAT Product Ratios of the IPL VGO with DA-300

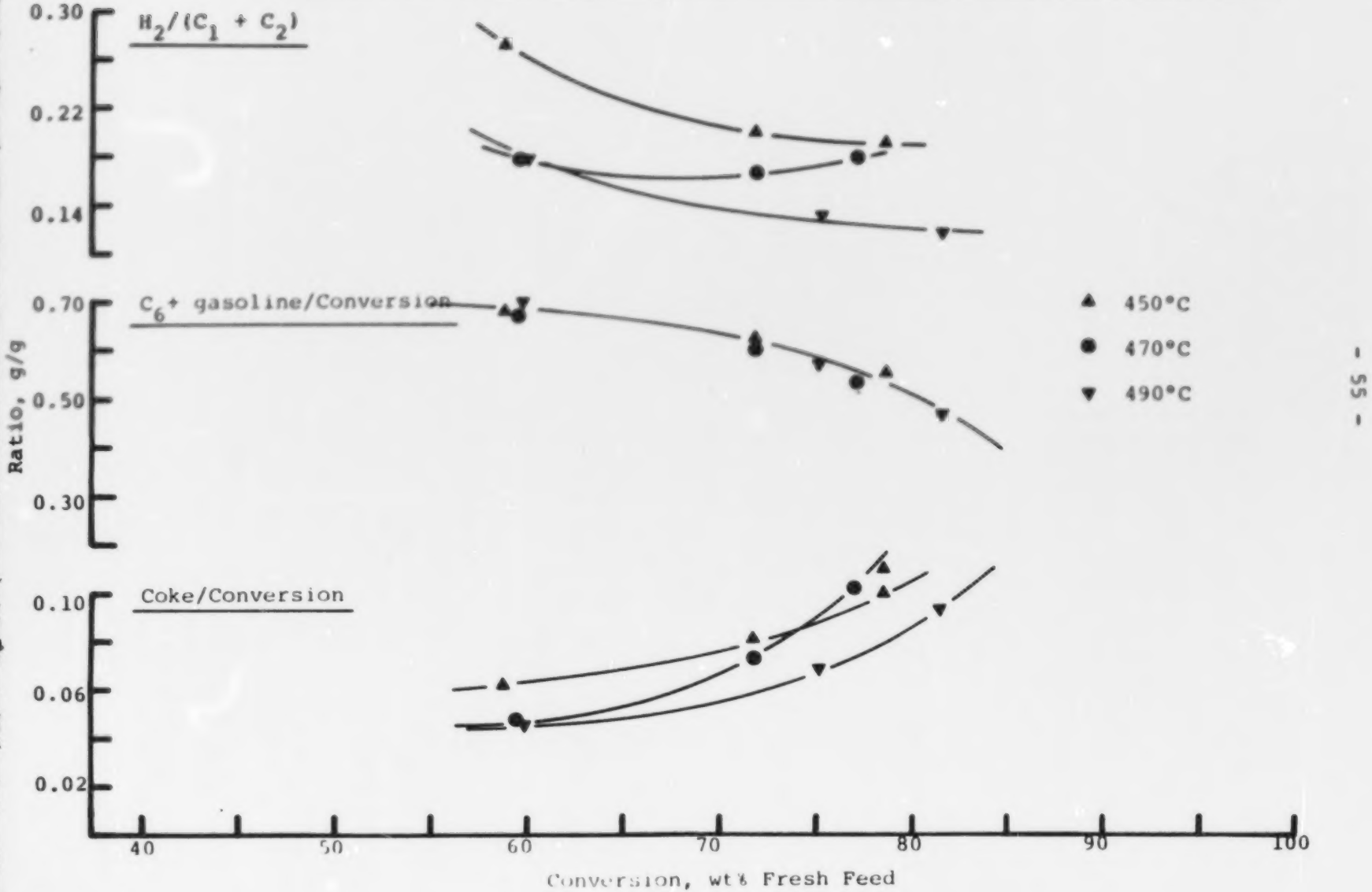


TABLE 4.6

Summary of Regression Analyses for IPL VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE
H_2	-0.3260		0.0090				0.8523	0.0355
ΣC_2	35.5657	-0.04724	-0.8417	0.0009		0.00369	0.9955	0.0864
ΣC_3	42.6239	-0.06996	-0.9171	0.0013		0.00341	0.9929	0.1881
ΣC_4	21.8755	0.0142	-0.8641			0.00834	0.9840	0.4235
ΣC_5	55.8706		-1.6745			0.0136	0.9603	0.4543
C_6+ gaso.	495.2830	-2.9297	6.9586	-0.00395	0.00339	-0.03675	0.9969	0.1998
LCO	64.8800	-0.03939	-0.4042				0.9550	0.9340
DO	34.9255	0.03947	-0.5932				0.9766	0.9370

Coke Yield (wt.%) = 5.96 + 1.146 (C/O) - 0.0130(T) — 0.27

Conversion (wt.%) = -2.456 + 11.78 (C/O) + 0.0732 (T) - 0.7173 $(C/O)^2$ — R^2 = 0.9868, Root MSE = 0.29

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

5) MAT PRODUCT DATA FOR VACUUM GAS OILS AND DA-300

To complete the base case evaluation so that residuum cracking with various feedstocks can be assessed, Syncrude and Lloydminster vacuum gas oils were also cracked on the microactivity test apparatus with DA-300. MAT product yields for these gas oils and catalyst are found in Tables 2.4 and 2.5, respectively. The relationships between conversion and C/O ratio (Figures 5.1 and 5.5) coke and C/O ratio (Figures 5.2 and 5.6), product yields and conversion (Figures 5.3 and 5.7) and selectivities and conversion (Figures 5.4 and 5.8) have been graphically presented. Results with DA-300 catalyst can be compared to show the effect of feedstock characteristics on cracking yields.

MAT experiments done at C/O ratios of 3-7 and T=450-490°C gave conversions of up to 81, 72 and 70 wt.% for IPL, Lloydminster and Syncrude vacuum gas oils. For the IPL feedstock, conversion increased approximately 3 wt.% over the temperature range at constant C/O ratio. Lloydminster gas oil gave a similar conversion increase with temperature while Syncrude vacuum gas oil had only a 2.5 wt.% increase under the same conditions. Conversion data for Syncrude vacuum gas oil at 425°C indicated that increasing reactor temperature to 450°C increases conversion 5-10 wt.%. This large increase, coupled with other work which showed not all heavy liquid products were removed from the catalyst during the MAT experiment at 425°C, led to the decision to use 450°C as the minimum operating temperature. Comparison of conversion-C/O ratio relationships for IPL, Lloydminster and Syncrude vacuum gas oils shows that only the Syncrude material appears to be approaching a maximum conversion asymptotically at C/O ratios greater than 5.5. The extent of conversion, the effect of temperature on conversion and the response of conversion to C/O ratio, indicate Syncrude vacuum gas oil is the most difficult feedstock to catalytically crack. Lloydminster vacuum gas oil is somewhat better, while IPL vacuum gas oil is the best fluid catalytic cracking feedstock evaluated. These results parallel those predicted from the evaluation of physical and compositional properties discussed previously.

Graphical analysis of data for IPL vacuum gas oil and Super DX, GRZ-1 and DA-300 catalysts had shown a wide range of coke selectivities. For the expression

$$\text{coke} = m\,(C/O) + b$$

the slope, m, or the coke selectivity had ranged from 0.9091 for Super DX at 475°C to 1.849 for GRZ-1 at 490°C. IPL vacuum gas oil and DA-300 catalyst gives the following coke-C/O ratio relationships:

$$\text{coke} = 1.043\,(C/O) + 0.59 \qquad T = 450°C$$
$$\text{coke} = 1.330\,(C/O) - 1.11 \qquad T = 470°C$$
$$\text{coke} = 1.121\,(C/O) - 0.354 \qquad T = 490°C$$

Lloydminster vacuum gas oil also gives very similar coke responses to C/O ratio:

$$\text{coke} = 1.022\,(C/O) - 0.127 \qquad T = 450°C$$
$$\text{coke} = 0.968\,(C/O) + 0.084 \qquad T = 470°C$$
$$\text{coke} = 1.091\,(C/O) - 1.022 \qquad T = 490°C$$

as does Syncrude vacuum gas oil:

$$\text{coke} = 1.167\,(C/O) - 0.700 \qquad T = 425°C$$
$$\text{coke} = 1.167\,(C/O) - 1.04 \qquad T = 450°C$$
$$\text{coke} = 1.079\,(C/O) - 0.59 \qquad T = 470°C$$
$$\text{coke} = 1.198\,(C/O) - 1.246 \qquad T = 490°C$$

The coke selectivities or slopes are remarkably similar, reflecting perhaps that, for gas oils, coke laydown is more a function of catalyst than of feedstock. The slightly reduced slopes for the Lloydminster case are likely due to the low Conradson carbon content and boiling range of this material. The consistency of the Syncrude coke selectivity is also remarkable, since it is virtually unaffected by temperature over a 65°C range of reactor temperature. This no doubt can be attributed to its unique aromatic composition, which makes it a difficult feedstock to crack and therefore to form coke.

Liquid product yields as well as conversion data suggest that Syncrude, Lloydminster and IPL vacuum gas oils are successively better feedstocks. Syncrude vacuum gas oil gives a maximum C_6+ gasoline yield of 38.6 wt.% at 62.5 wt.% conversion. This corresponds to maximum C_6+ gasoline yields of 38.6 and 45.5 wt.% for Lloydminster and IPL vacuum gas oil at 65 and 73% conversions, respectively. Clearly, IPL vacuum gas oil is capable of producing significantly more gasoline than either Lloydminster or Syncrude VGOs.

The same order of feedstock quality also occurs when total liquid yields are compared. This is the sum of C_3s, C_4s, C_5s, C_6+ gasoline and light cycle oil. These can be considered liquid products since olefinic light ends are oligomerized to form gasoline blending components, light cycle oil can be hydrotreated and blended into middle distillate fuels and butanes and pentanes are used in gasolines. At maximum gasoline yield, IPL vacuum gas oil produces the largest total liquid product yield, 82.3 wt.%, which is composed of 13 wt.% C_3 C_4s, 6.3 wt.% C_5s, 45.5 wt.% C + gasoline and 18 wt.% light cycle oil. Lloydminster vacuum gas oil gives 5.1 wt.% lower total liquid product yield, 77.7%, which is made up of smaller yields of LPGs (12.5 wt.% C_3 C_4s, 5.8 wt.% C_5s) and gasoline (38.6 wt.% C_6+ gasoline) but a larger yield of light cycle oil (20.8 wt.%). These trends continue with Syncrude vacuum gas oil liquid product yields. Although total liquid yield is 79.5 wt.%, slightly greater than that of Lloydminster vacuum gas oil, the LPGs (12 wt.% C_3 C_4s, 5 wt.% C_5s) and gasoline (38.0 C_6+ gasoline) yields are reduced while light cycle oil yields (24.5 wt.%) are significantly higher.

Increased severity of cracking for all vacuum gas oils results in increased yields of light ends, LPGs and coke while reducing the yields of light cycle and decant oil. For both IPL and Lloydminster VGOs the yield of C_6+ gasoline as a function of conversion occurs with a sharp maxima while for Syncrude it is a very shallow maxima. In fact, all Syncrude yields change only very gradually with conversion, which indicates that it is a difficult feedstock to crack. The LCO yield for Syncrude is also most unusual, since it goes through a maxima at 45% and perhaps offers an option for

maximizing middle distillate yields.

Product yields were also statistically fit to operating variables T, C/O and conversion (Tables 5.2 and 5.4) for MAT product yields obtained from DA-300 and Syncrude and Lloydminster vacuum gas oils, respectively. Fits for conversion and product yields were very good and gave rise to low values for root mean square error which were generally for less than the experimental error anticipated. This indicated that the experimental data is of good quality. The coke yield data for Syncrude vacuum gas oil and DA-300 regressed to a linear equation in temperature while the Lloydminster data regression contained temperature terms. Such behaviour illustrated the affect feedstock had on coke yield and was observed graphically. For both these feeds, conversion was a complicated function of both temperature and C/O ratio with root mean square errors of 2.5 and 1.7% relative, respectively. All other product yields were fit to the best temperature-conversion quadratic surface.

The data discussed in this section will form the basis for evaluating resid cracking in following sections.

TABLE 5.1

MAT Product Yield Data for Syncrude Vacuum Gas Oil and Davison DA-300

est	MAT 236	MAT 235	MAT 272	MAT 271	MAT 269	MAT 234	MAT 227	MAT 228	MAT 268	MAT 270
ass Balance, wt%	99.6	99.7	101.9	100.5	99.3	97.9	99.5	104.4	101.9	100.8
, °C	427	427	425	428	452	448	446	448	452	450
/O, g/g	1.83	3.20	5.50	7.92	1.44	3.08	6.49	6.28	7.25	7.44
ields, wt% FF										
H_2	0.12	0.14	0.31	0.36	0.09	0.17	0.33	0.30	0.35	0.40
CH_4	0.05	0.07	0.17	0.31	0.06	0.12	0.29	0.36	0.55	0.59
ΣC_2	0.43	0.64	1.00	1.59	0.33	0.85	1.52	1.73	2.23	2.33
ΣC_3	1.07	1.65	3.68	4.15	1.43	2.43	3.73	4.00	5.05	5.12
ΣC_4	2.16	3.52	7.53	8.22	2.82	4.40	7.61	7.02	9.32	9.43
ΣC_5	1.73	2.43	3.83	4.54	1.33	3.23	4.89	4.92	5.63	5.44
C_5+ gasoline	21.5	27.3	37.0	40.2	18.6	36.5	41.7	43.2	43.3	42.3
C_6+ gasoline	19.8	24.9	33.2	35.7	17.3	33.2	36.8	38.2	37.6	36.9
LCO	20.0	25.0	24.0	22.5	16.9	32.0	24.6	23.7	20.2	20.0
DO	53.3	39.1	20.8	15.2	58.8	21.3	15.4	14.2	13.1	12.7
Coke	1.65	2.75	5.94	8.16	1.13	2.57	5.43	6.28	6.88	8.13
Conversion	26.8	35.9	55.2	62.3	24.3	46.7	60.0	62.2	66.8	67.3
C_6+ gasoline/Conversion	0.739	0.694	0.601	0.573	0.712	0.711	0.613	0.614	0.563	0.548
Coke/Conversion	0.0616	0.0766	0.108	0.131	0.0465	0.0550	0.0905	0.101	0.103	0.121
C_6+ gasoline/coke	12.0	9.06	5.56	4.37	15.3	12.9	6.77	6.08	5.47	4.53

TABLE 5.1 Cont'd

MAT Product Yield Data for Syncrude Vacuum Gas Oil and Davison DA-300

Test	MAT 263	MAT 262	MAT 232	MAT 233	MAT 383	MAT 382	MAT 381
Mass Balance, wt%	98.9	101.5	106.8	102.9	100.3	102.4	102.1
T, °C	473	474	471	473	491	493	491
C/O, g/g	1.63	3.50	6.04	7.91	2.87	4.79	7.10
Yields, wt% FF							
H_2	0.14	0.21	0.31	0.40	0.24	0.30	0.40
CH_4	0.13	0.26	0.53	0.70	0.32	0.54	0.94
ΣC_2	0.66	1.28	2.04	2.76	1.33	2.01	3.10
ΣC_3	2.04	3.18	4.19	5.82	3.45	4.66	5.80
ΣC_4	3.48	5.60	7.16	9.54	5.85	7.92	9.71
ΣC_5	1.66	3.64	5.12	7.15	3.56	5.19	6.56
C_5+ gasoline	25.1	38.5	41.9	42.4	37.8	41.9	43.8
C_6+ gasoline	23.4	34.9	36.8	35.2	34.2	36.7	37.2
LCO	20.0	23.5	23.4	20.1	22.0	21.5	17.8
DO	47.4	24.9	15.1	11.3	27.2	17.7	12.4
Coke	1.35	3.00	6.22	8.07	2.40	4.30	7.46
Conversion	32.6	51.6	61.6	68.6	50.8	60.8	69.9
C_6+ gasoline/Conversion	0.718	0.676	0.597	0.513	0.673	0.604	0.532
Coke/Conversion	0.0414	0.0581	0.101	0.118	0.0472	0.0707	0.107
C_6+ gasoline/coke	17.3	11.6	5.91	4.35	14.3	8.54	4.97

FIGURE 5.1

The Effect of C/O Ratio on Conversion for Syncrude VGO and DA-300

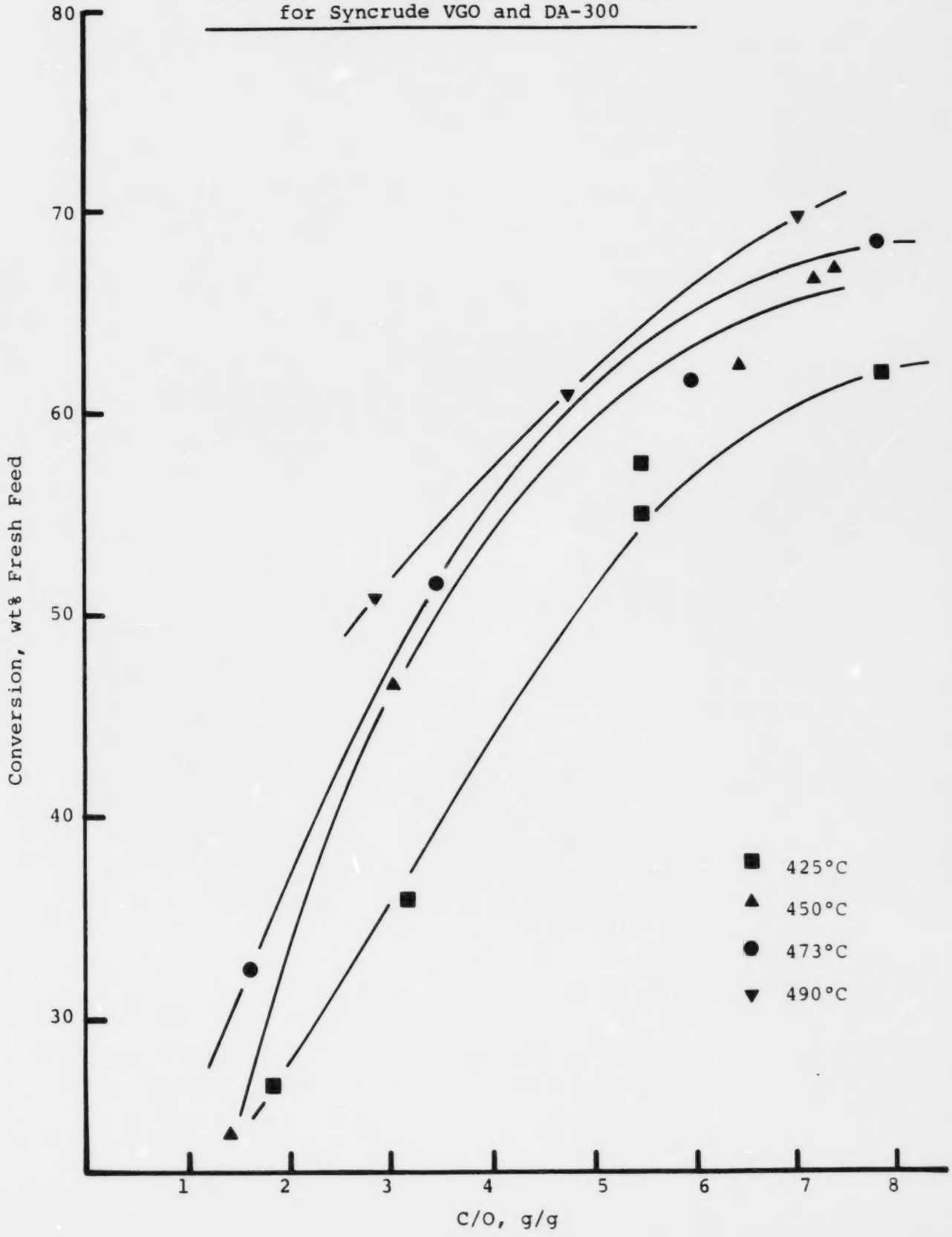


FIGURE 5.2

The Dependence of Coke Yield on C/O Ratio for Syncrude VGO and DA-300

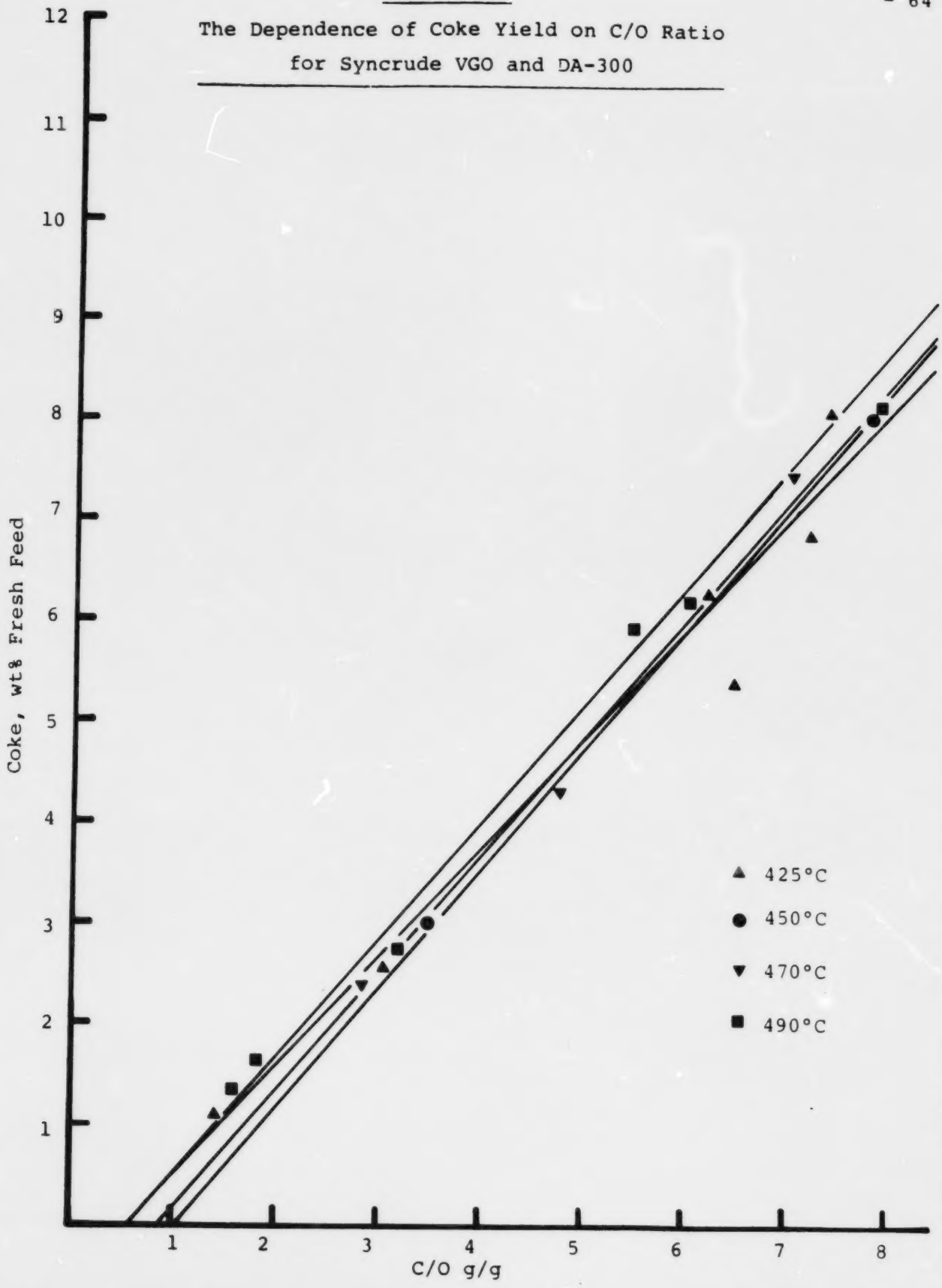


FIGURE 5.3

The Effect of Conversion on MAT Product Yields of Syncrude VGO with DA-300

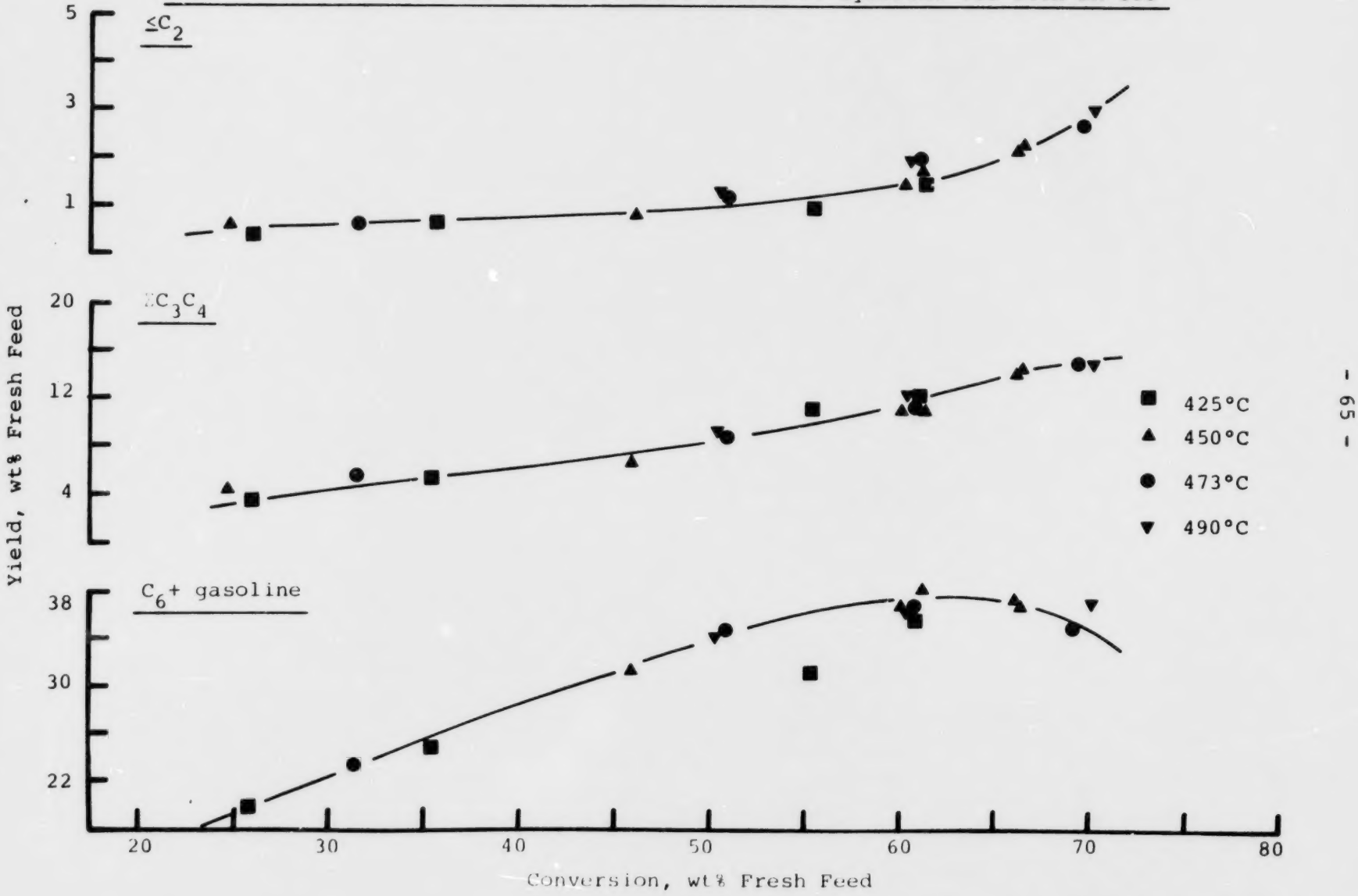


FIGURE 5.3 (continued)

The Effect of Conversion on MAT Product Yields of Syncrude VGO and DA-300 (continued)

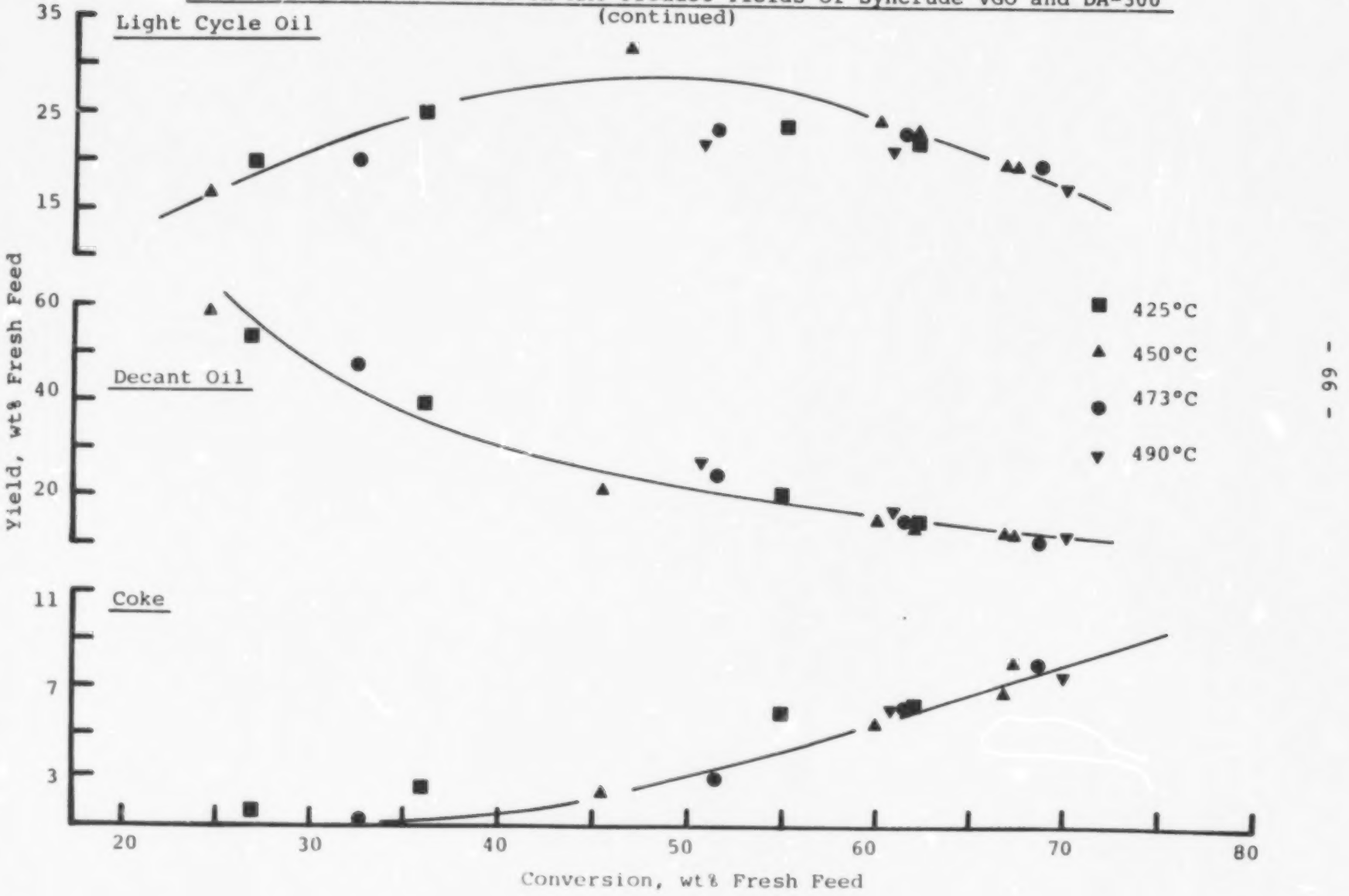


FIGURE 5.4

The Effect of Conversion on MAT Product Ratios of Syncrude VGO with DA-300

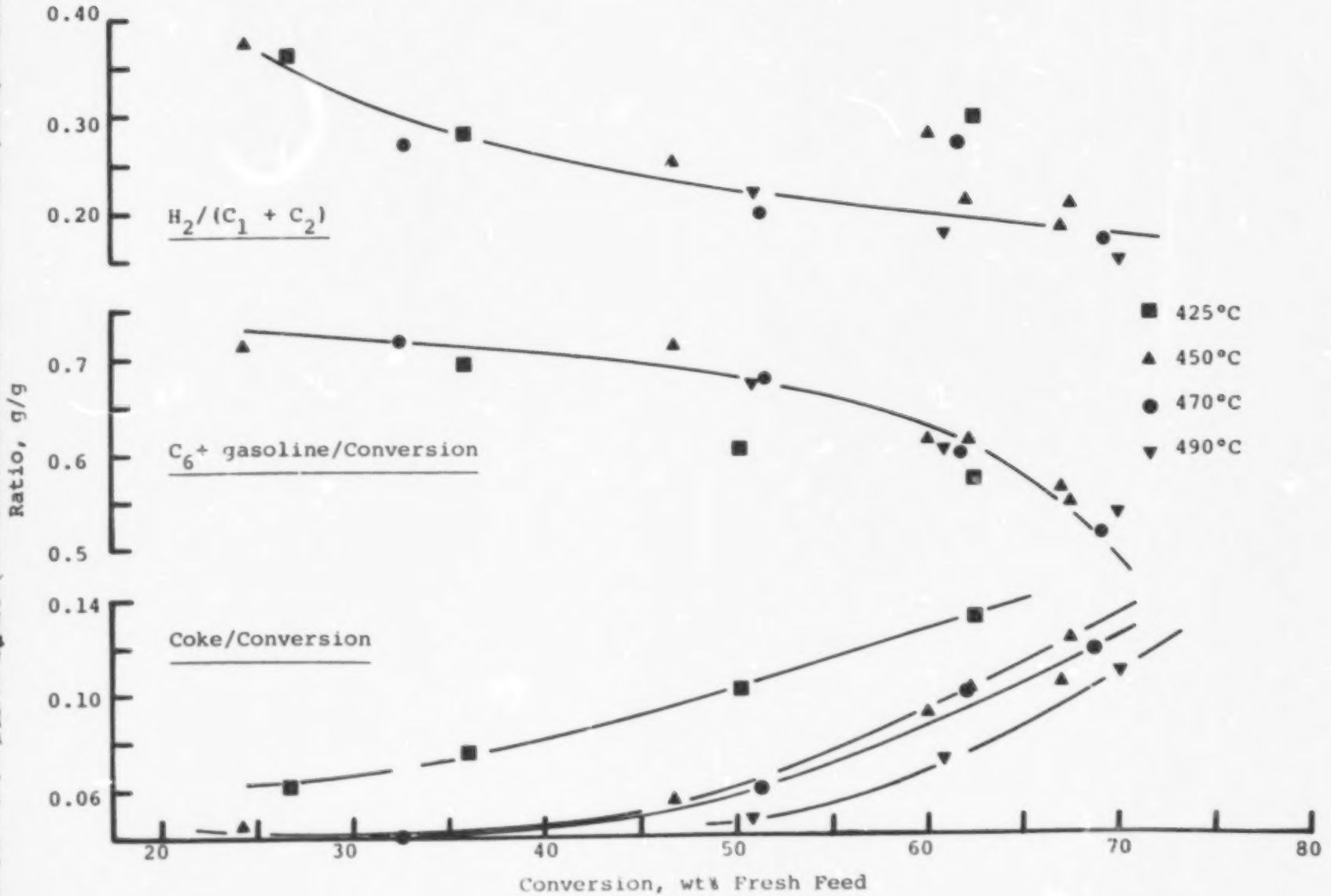


TABLE 5.2

Summary of Regression Analyses for Syncrude VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE %
H_2	6.5543	-0.0299	0.01466	-4.7743E-05	3.4958E-05	0.0001469	0.9798	0.0180
ΣC_2	3.6454		-0.2208	0.0003434	-1.1127E-05	0.001176	0.9877	0.1047
ΣC_3	-1.8763			-0.0001592	1.9945E-05	0.001714	0.9817	0.2220
ΣC_4	125.5320	-0.5931	0.4187	-0.001272	0.0007191	0.003377	0.9806	0.4196
ΣC_5	9.9800		-0.3984	0.0008856	-4.5849E-05	0.001109	0.9785	0.2884
C_6+ gaso.	-11.5564		1.4324			-0.01058	0.9783	0.0524
LCO	-492.3816	2.3340		0.004208	-0.002841	-0.01977	0.8539	1.5182
DO	683.5809	-2.8500		-0.006628	0.003545	0.02079	0.9922	1.5655

Coke Yield (wt.%) = -0.600 + 1.091 (C/O) — R^2 = 0.9763, Root MSE % = 0.41

Conversion (wt.%) = -68.57 + 13.49 (C/O) + 0.1716 (T) - 0.7974 $(C/O)^2$ — R^2 = 0.9776, Root MSE % = 2.47

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

TABLE 5.3

MAT Product Yield Data for Lloydminster Vacuum Gas Oil and DA-300

Test	MAT 364	MAT 366	MAT 369	MAT 365	MAT 367	MAT 368	MAT 370	MAT 371	MAT 372
Mass Balance, wt%	99.5	99.5	99.5	99.6	99.5	99.4	99.5	99.5	99.5
T, °C	449	450	450	469	471	468	491	491	492
C/O, g/g	2.47	4.81	7.07	2.63	4.66	8.01	3.39	5.22	8.09
Yields, wt% FF									
H_2	0.08	0.25	0.42	0.15	0.29	0.50	0.25	0.45	0.64
CH_4	0.10	0.23	0.39	0.18	0.37	0.62	0.37	0.63	1.01
ΣC_2	1.49	2.46	3.22	1.65	2.64	3.76	2.61	3.67	4.88
ΣC_3	2.25	4.39	5.24	3.03	4.71	6.00	4.89	6.06	6.88
ΣC_4	3.72	8.22	9.96	5.50	8.85	11.1	7.93	10.5	11.9
ΣC_5	2.69	5.76	6.70	3.38	5.87	8.59	5.78	6.39	9.39
C_5+ gasoline	36.4	43.5	44.1	41.1	44.7	43.3	43.9	42.7	42.5
C_6+ gasoline	33.7	37.7	37.4	37.7	38.8	34.8	38.1	36.3	33.1
LCO	24.9	22.3	19.4	24.1	21.1	17.7	21.3	19.5	16.4
DO	28.9	14.1	11.1	22.2	13.5	10.5	16.6	13.1	9.82
Coke	2.35	5.06	6.99	2.44	4.61	7.60	2.77	4.42	7.68
Conversion	46.2	63.6	69.5	53.7	66.5	71.8	62.1	67.0	73.8
C_6+ gasoline/Conversion	0.729	0.593	0.538	0.702	0.592	0.485	0.614	0.542	0.449
Coke/Conversion	0.0509	0.0796	0.101	0.0454	0.0704	0.106	0.0446	0.0660	0.104
C_6+ gasoline/coke	14.3	7.45	5.33	15.5	8.41	4.58	13.8	8.21	4.32

FIGURE 5.5

The Effect of C/O Ratio on Conversion for Lloydminster VGO and DA-300

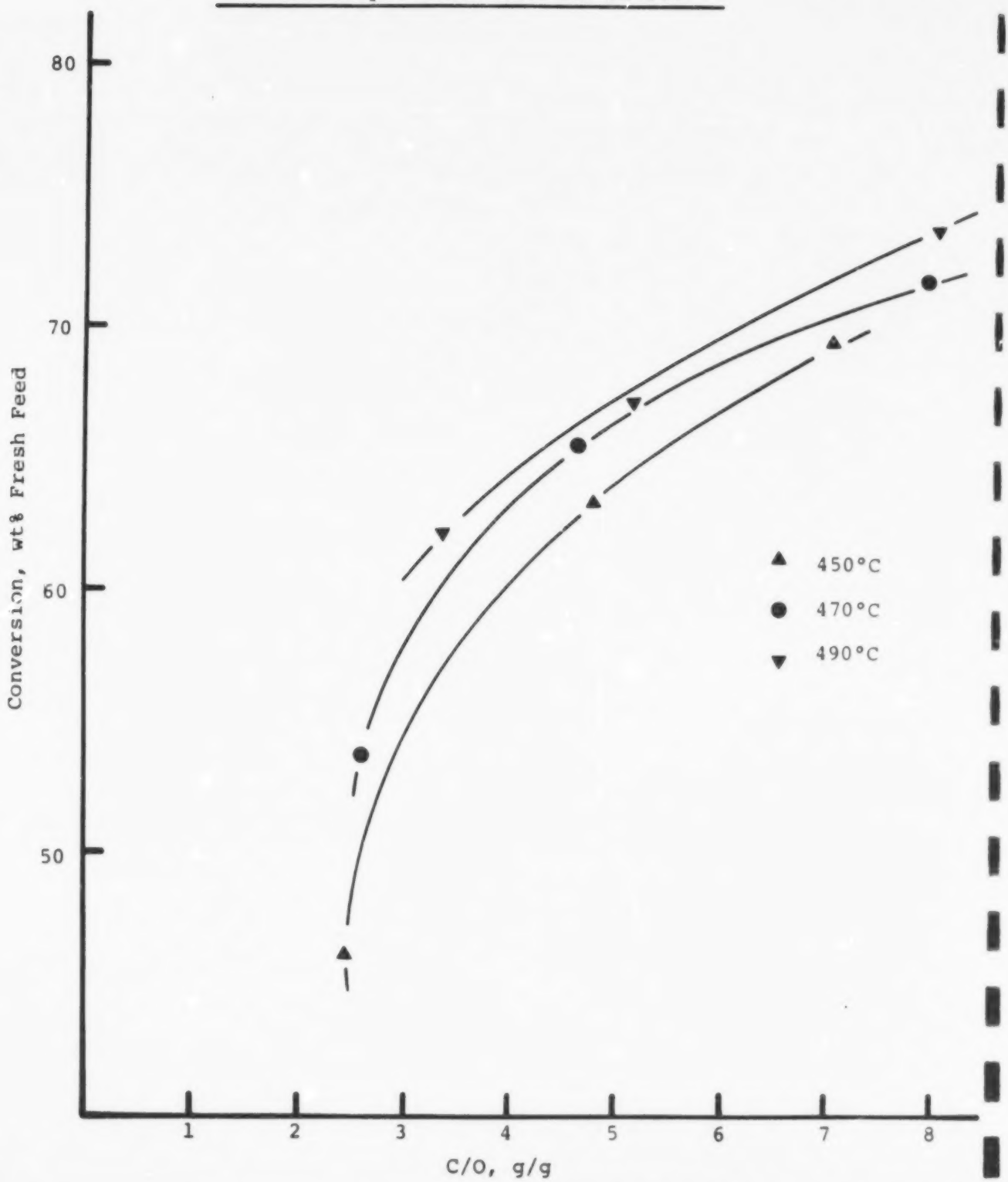


FIGURE 5.6

The Dependence of Coke Yield on C/O Ratio for Lloydminster VGO and DA-300

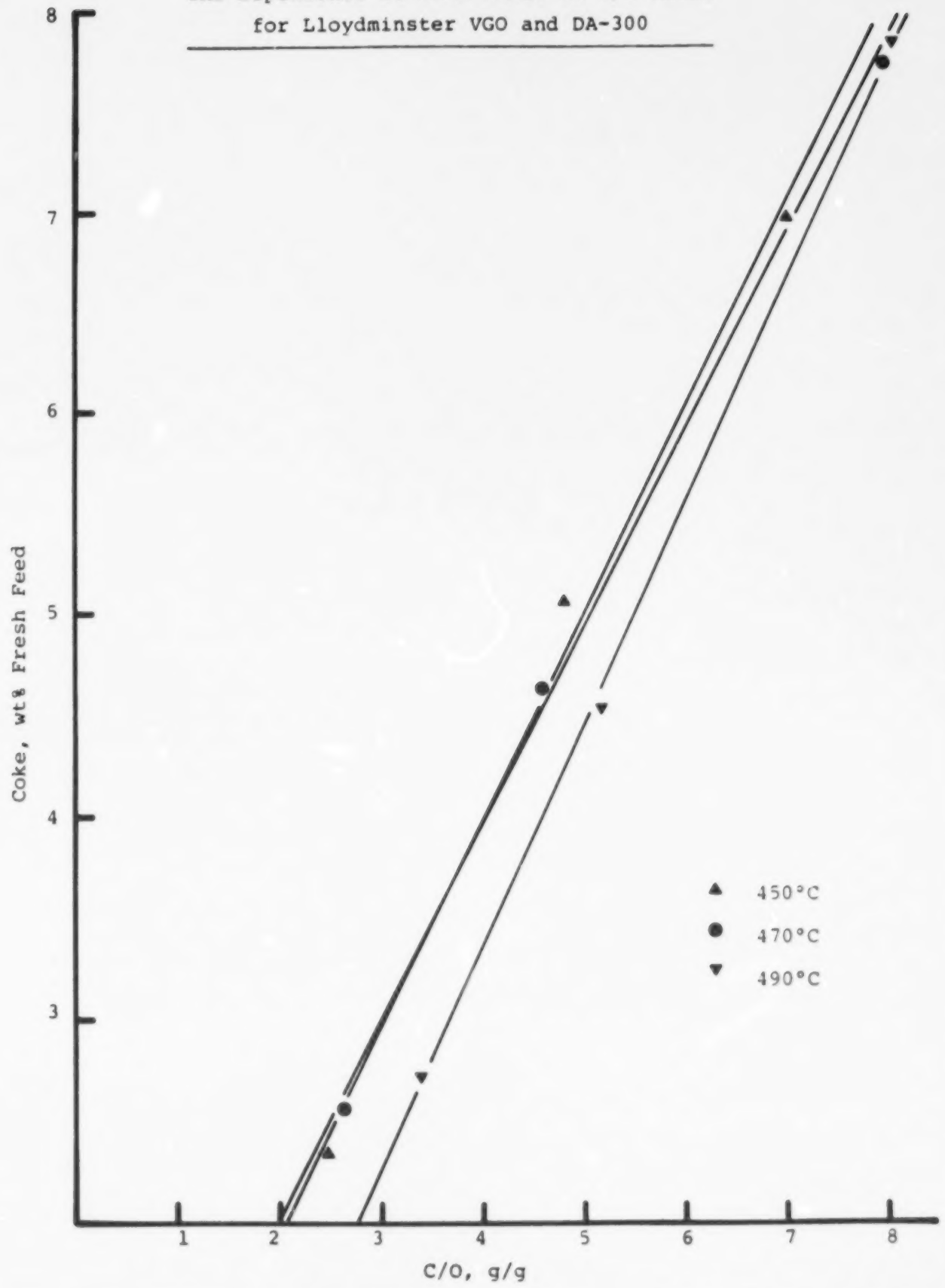


FIGURE 5.7

The Effect of Conversion on MAT Product Yields of Lloydminster VGO with DA-300

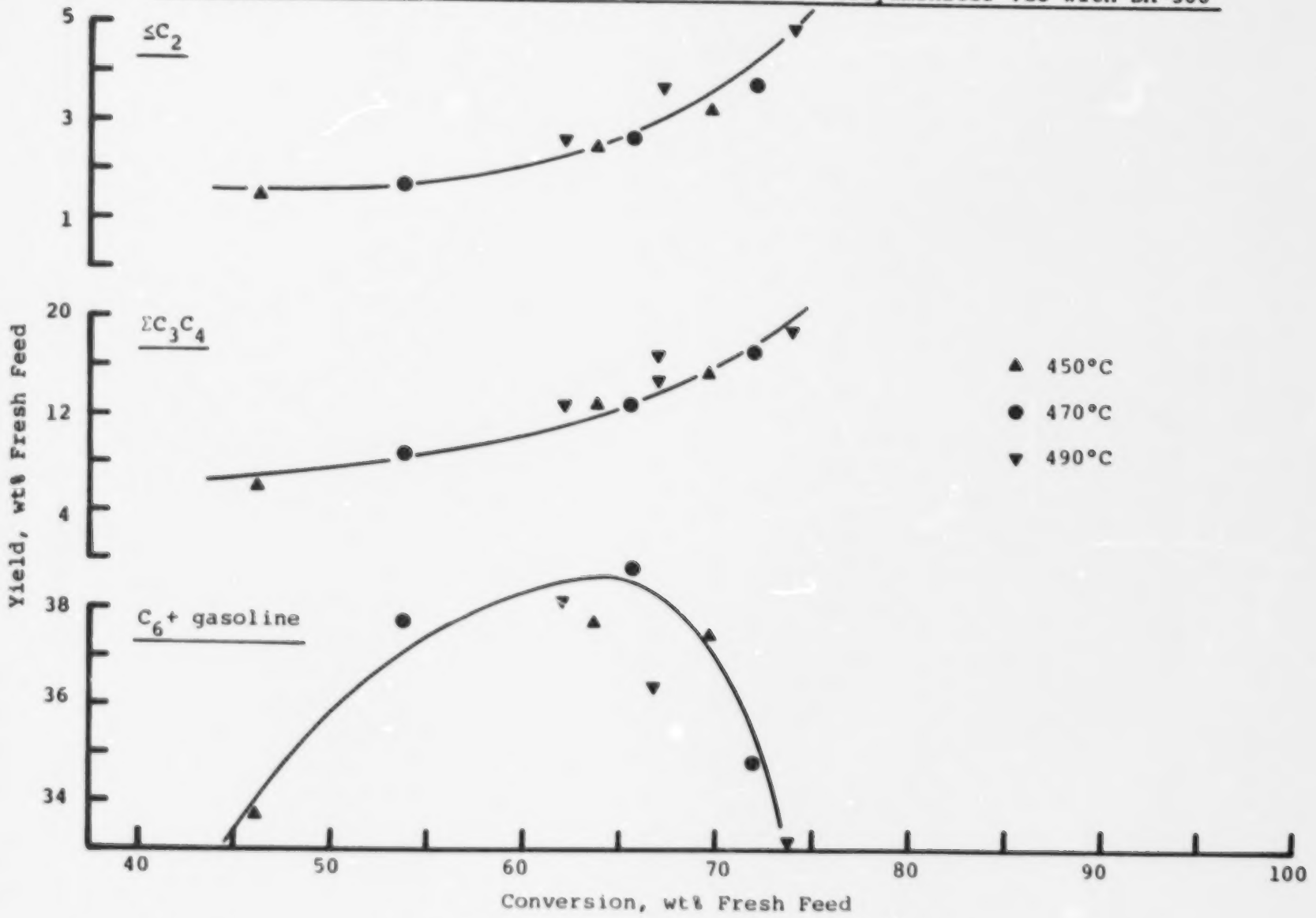


FIGURE 5.7

The Effect of Conversion on MAT Product Yields of Lloydminster VGO with DA-300
(continued)

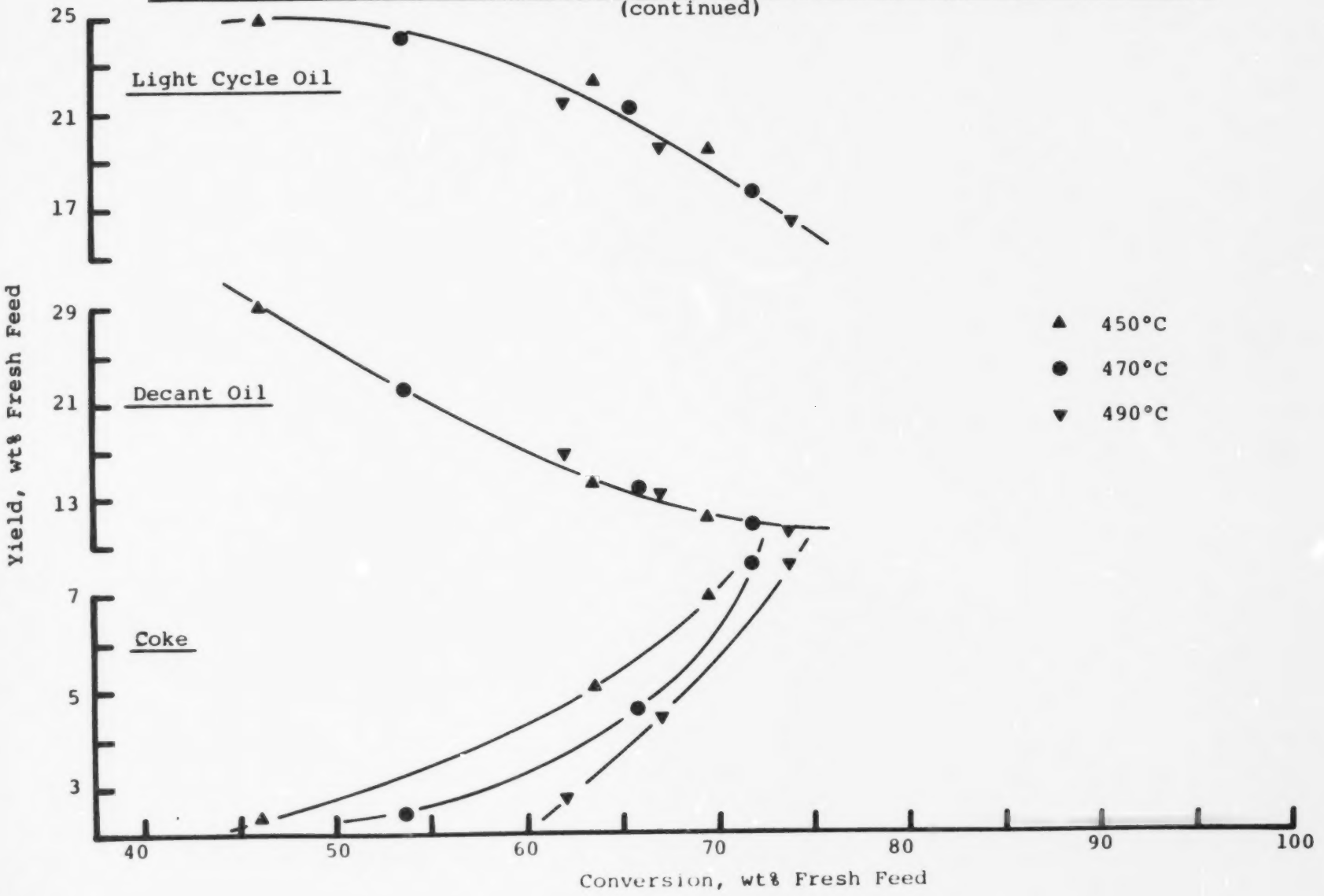


FIGURE 5.8

The Effect of Conversion on MAT Product Ratios of Lloydminster VGO with DA-300

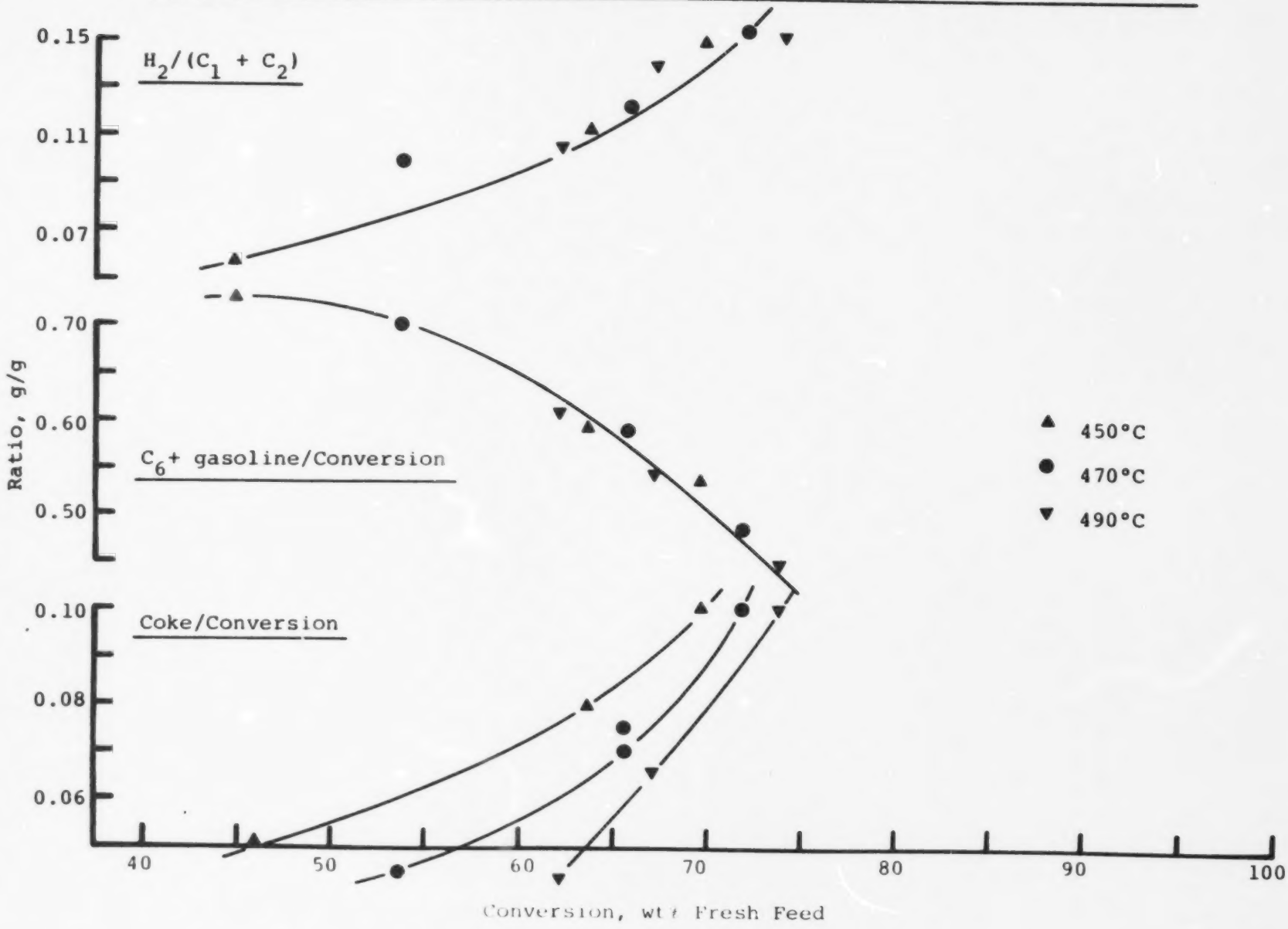


TABLE 5.4

Summary of Regression Analyses for Lloydminster VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE %
H_2	1.6938		-0.0810		1.9302E-06	0.0008176	0.9780	0.0336
ΣC_2	137.7076	-0.5450	-0.4672		0.0005956	0.004703	0.9894	0.1564
ΣC_3	154.2835	-0.6779			0.0007425	0.001192	0.9818	0.1939
ΣC_4	-1.5846					0.002476	0.9788	0.4147
ΣC_5	14.6381		-0.5641			0.006629	0.9961	0.4558
C_6+ gaso.	-55.3397		-3.1367			-0.02619	0.8780	0.8288
LCO	41.7251			0.003633	-0.0002846	-0.01624	0.9966	0.2065
DO	70.4623		-1.3461	-0.002637	0.0002113	0.001531	0.9997	0.1498

Coke Yield (wt.%) = 6.65 + 1.00 (C/O) - 0.01472 (T) 0.21

Conversion (wt.%) = -104.92 + 25.05 (C/O) + 0.2894 (T) - 0.0322 (C/O)(T) - 0.5980 $(C/O)^2$ 0.9817 1.67

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

6) THE EFFECT OF IPL VTB ON MAT PRODUCT YIELDS

IPL vacuum tower bottoms (VTB) at four successively greater concentrations were blended into IPL vacuum gas oil at levels ranging from 8.4 to 33.7 wt.% VTB. The highest level of VTB addition corresponds to a feedstock which is 94 wt.% ATB and only 6% VGO and has a Conradson carbon content of 7.0 wt.%. The four blended feedstocks were cracked on the microactivity test unit at 490°C and 4 C/O ratio, the conditions for maximum gasoline with IPL VGO and DA-300. MAT product yields for these blends and IPL VGO at the above conditions are listed in Table 6.1. Product yields are also shown graphically as a function of VTB feedstock concentration in Figure 6.1.

Results in Table 6.1 clearly show the effect VTB has on MAT product yields. Over the range of VTB additions studied, (0-33.7 wt.%) hydrogen, methane, total light ends, C_3s, C_4s, C_5s and coke yields were seen to increase 57, 145, 89, 27, 16, 24 and 93.1% with increasing VTB addition, while C_5+ gasoline yields decreased 6% in absolute terms and 12% relatively. Light cycle oil and decant oil yields decreased only slightly with increased VTB concentrations in the feedstocks. Since conversion is defined as 100-LCO-DO, the net effect is to increase conversion slightly. Overall, the addition of IPL VTB to VGO causes an increase in the amount of coke and gases produced at the expense of C_6+ gasoline yield.

The data in Table 6.1 can also be used to calculate pure VTB product yields assuming the yields of the individual feedstock components are additive. While some yields do not correlate, particularly at low VTB levels where all experimental errors will be greatly exaggerated, results in Table 6.2 show that the calculated VTB product yields are relatively constant over the range of VTB/VGO feedstocks evaluated. IPL VTB coke yield was remarkably constant in the range of 13.8 to 14.9 wt.% and was 3.75 times greater than that of IPL VGO. C_5+ gasoline yield was reduced 6.5 to 7.5 wt.% at VTB feed concentrations of 8.4 to 25.3 wt.%. With 33.7 wt.% VTB in the feed, C_5+ gasoline yield fell 17.1 wt.%. Such a huge loss in gasoline yield may be due to excessive coke laydown on the catalyst, which was held constant for

these experiments. Gas yields for VTB calculated from 8.4 wt.% VTB feeds are unreasonably high, particularly when compared with yields from other feeds. Similarly, the cycle oil yields for 8.4 wt.% feed are negative, reflecting the magnification of inherent experimental error into unreasonable yields. Nevertheless, yield data calculated for IPL VTB are reasonably consistent and confirm this material, relative to its VGO, produces more gases and coke and less C_5+ gasoline and light cycle oil. While it is not surprising VTB is not as good a feedstock as its corresponding VGO, it is encouraging to note (Table 3.2), some 70 wt.% of it is upgraded to liquid fuels.

Coke yield data indicate that coke formation may cause thermal problems in a commercial unit. Assuming no limitation on blower capacity, the temperature of a commercial unit regenerator was estimated from heat balance calculations (Appendix 1). These results show that the mixture of 33.7% VTB could be processed and still maintain the regenerator at its upper limit of operability (1450°F). The mixture of 33.7 wt.% VTB/66.3 wt.% VGO was then used in a 3x3 factorial design experiment to evaluate the effects of VTB cracking over the same temperature and C/O range already established for VGO. These two sets of data will allow any IPL VTB/VGO mixture up to 33.7 wt.% VTB to be estimated by interpolation, since the above results indicate this approach is valid.

TABLE 6.1

MAT Product Yields for IPL VTB/VGO Mixtures & DA-300

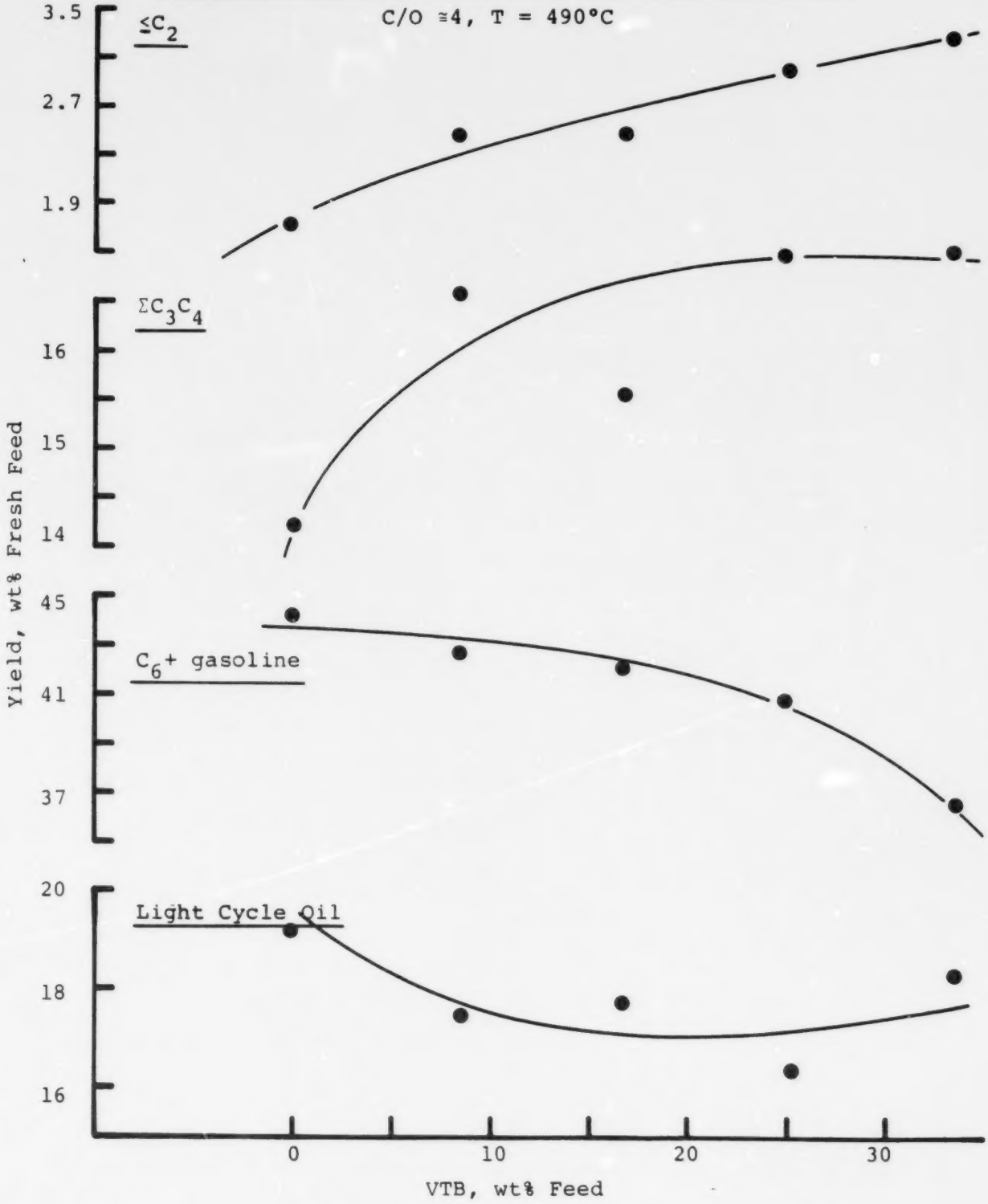
Test	MAT 384	MAT 385	MAT 386	MAT 387	MAT 388
Mass Balance, wt%	102.7	99.8	99.3	102.4	101.2
T, °C	491	490	490	489	490
C/O, g/g	4.15	4.08	4.10	4.26	4.28
Feed Composition, wt%					
ATB (1)	0	23.5	47	70.5	94.0
VTB	0	8.4	16.9	25.3	33.7
VGO	100	91.6	83.1	74.7	66.3
Product Yields, wt%					
H_2	0.28	0.41	0.37	0.41	0.44
CH_4	0.44	0.68	0.73	0.99	1.08
$\leq C_2$	1.74	2.46	2.50	3.07	3.28
ΣC_3	5.00	5.96	5.62	6.27	6.33
ΣC_4	9.23	10.6	9.96	10.7	10.7
ΣC_5	5.97	6.72	6.48	7.38	7.40
C_5+ gasoline	50.1	49.4	48.6	48.3	44.1
C_6+ gasoline	44.2	42.7	42.2	40.9	36.7
LCO	19.2	17.5	17.8	16.4	18.3
DO	10.9	9.37	9.93	8.63	9.97
Coke	3.81	4.66	5.49	6.61	7.36
Conversion	69.9	73.2	72.2	75.0	71.8
C_6+ gasoline/Conversion	0.632	0.583	0.584	0.545	0.511
Coke/Conversion	0.0545	0.0636	0.0760	0.0881	0.103
C_6+ gasoline/coke	11.6	9.16	7.68	6.19	4.96

(1) 35.9 wt.% VTB in VGO is ATB for IPL

FIGURE 6.1

The Effect of IPL VTB Concentration on MAT
Product Yields for IPL VTB/VGO Mixtures and DA-300

C/O ≅4, T = 490°C



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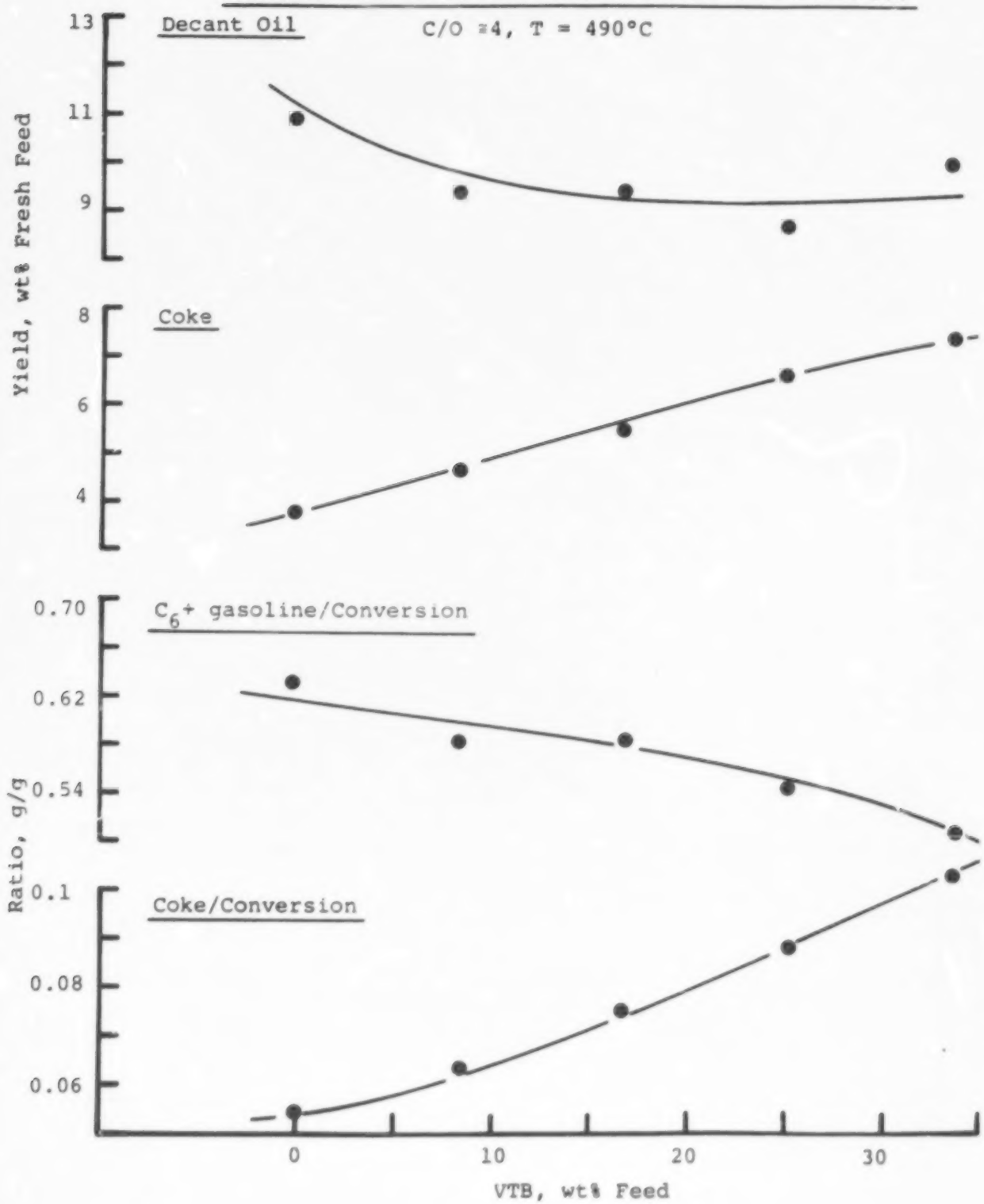
The Effect of IPL VTB Concentration on MAT Product Yields for IPL VTB/VGO Mixtures and DA-300



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The Effect of IPL VTB Concentration of
MAT Product Yields for IPL VTB/VGO Mixtures and DA-300

C/O ≈4, T = 490°C

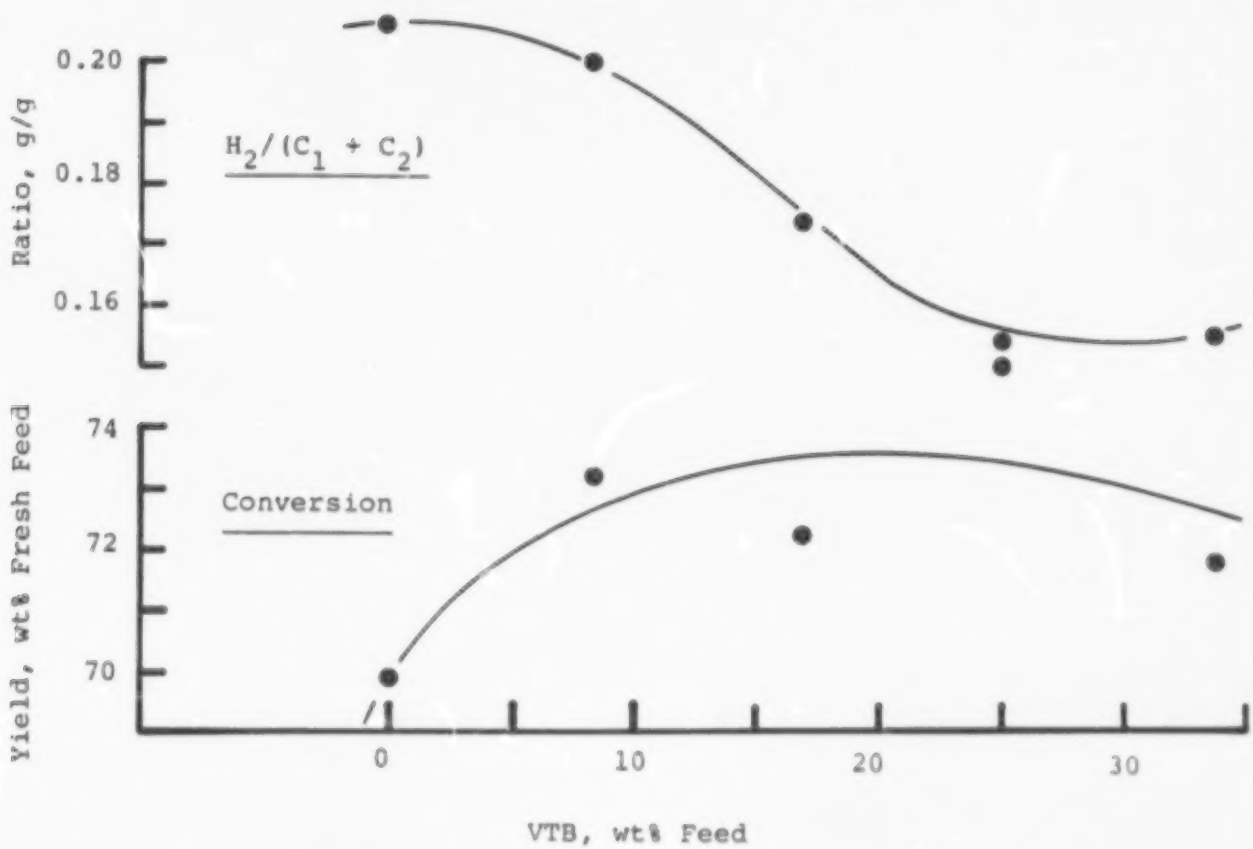


TABLE 6.2

Calculated IPL VTB Product Yields with DA-300*
(T=490°C, C/O =4)

Material	VTB					VGO
Test	MAT 385	MAT 386	MAT 387	MAT 388	Average	MAT 384
Wt% VTB in Feed	8.4	16.9	25.3	33.7		
Product Yields, wt%						
H_2	1.82	0.61	0.79	0.75	0.72	0.28
CH_4	3.30	2.16	2.61	2.34	2.37	0.44
ΣC_2	10.3	6.24	7.00	6.31	6.52	1.74
ΣC_3	16.4	8.66	10.0	8.94	9.20	5.00
ΣC_4	25.5	13.5	15.0	13.6	14.0	9.23
ΣC_5	14.9	8.99	11.5	10.2	10.2	5.97
C_5+ gasoline	41.8	41.2	43.0	32.3	38.8	50.1
C_6+ gasoline	26.3	32.4	31.2	21.9	28.5	44.2
LCO	-1.0	10.9	8.13	16.5	11.8	19.2
DO	-7.3	5.16	1.92	8.14	5.07	10.9
Coke	13.9	13.8	14.9	14.3	14.2	3.81

*Calculated from the weight averaged composition
+Average of MAT 386, MAT 387 and MAT 388 VTB Product Yields

7) MAT PRODUCT YIELD DATA FOR IPL 33.7 wt.% VTB/ 66.3 wt.% VGO

A mixture of 33.7 wt.% IPL VTB in 66.3 wt.% IPL VGO was cracked at 3 C/O ratios for each of three temperatures. Experimental conditions and yield data for these tests are listed in Table 7.1. Data in Figure 7.1 show the effects of C/O ratio on conversion for IPL VTB/VGO as well as for IPL VGO. A comparison of data for the two feedstocks reveals that 1) conversion increases from 2.5 to 10 wt.% for the VTB/VGO at the same C/O ratio for $3<C/O<7$, 2) the response of conversion to temperature is similar (3-4 wt.% for C/O = 7 and T = 40°C), and 3) VTB/VGO conversion levels off asymptotically at 83 wt.% for C/O ratios of 5 or greater, while for VGO this occurs at greater C/O ratios and lower levels of conversion. With VTB/VGO feed, more non cycle oil products (gases, liquids and coke) are produced at the same temperature and C/O ratio than for VGO, which gives rise to the greater conversion. The fall off of conversion with C/O can be attributable to either catalyst fouling with coke or the exhaustion of convertible precursors in the feedstocks. Coke yields suggest this is due to the former.

Coke yield response to C/O ratio is also plotted in Figure 7.2. The relationship again appears to be linear as it was for the VGO. The best straight line relationships for VTB/VGO are:

coke, wt.% = 1.945 (C/O) + 1.05 T = 450°C
coke, wt.% = 1.278 (C/O) + 3.79 T = 470°C
coke, wt.% = 2.105 (C/O) - 0.64 T = 490°C

These compare with coke/(C/O) relationships for IPL VGO of:

coke, wt.% = 1.043 (C/O) + 0.59 T = 450°C
coke, wt.% = 1.330 (C/O) - 1.11 T = 470°C
coke, wt.% = 1.121 (C/O) - 0.354 T = 490°C

The coke/(C/O) equation for VTB/VGO at 470°C is odd in that the slope is less than that obtained for the VGO; however, the large intercept makes the coke yield greater over the range of C/O ratios studied. The latter relationship is likely too high and therefore these results should be disregarded and attributed to experimental noise. Results at

450 and 490°C show that the slope of the coke/(C/O) relationship is greater for the VTB/VGO mixture (1.95-2.11) than for the VGO (1.04-1.12). This increase in slope or coke selectivity is due to the greater coke-forming propensity of the feedstock which is in turn related to feedstock composition discussed previously The intercepts for VTB/VGO coke/(C/O) relationships are larger and more positive than those for VGO data. This may also indicate greater coking tendency of the feedstock since at C/O=0 no catalyst would be present and, if the feedstock was thermally stable, coke yield would also be zero. However if the feed was not thermally stable, the intercept would be positive and directly proportional to the degree of instability. Negative intercepts are difficult to explain except for experimental error.

Product yields and selectivities for the IPL 33.7 wt.% VTB/ 66.3 wt.% VGO mixture are shown as a function of conversion in Figures 7.3 and 7.4. Results confirm over the complete range of temperatures and C/O ratios studies what was observed with blends at 490°C and C/O ~4, i.e. when VTB is added to VGO feedstock, cracking yields change, light ends, C_3s, C_4s and coke yields increase; C_6+ gasoline and decant oil yields decrease, while LCO yield is similar and increases slightly. C_6+ gasoline yield decreases 2.3 wt.% for the mixture, and this is somewhat compensated for by a 1.8 wt.% increase in LCO. The decant oil yield decreases slightly by 1.5 wt.%; however, the coke yield increases by 2.5 to 4%. This is to be expected because of the larger concentration of DO + coke precursors in VTB.

Regression analysis of IPL VTB/VGO MAT product yields as functions of temperature, C/O ratio and conversion are summarized in Table 7.2. This data can be compared with that established for IPL VGO (Table 4.6). The comparison shows that while the VGO data set gave good fits for all product yields the VTB/VGO data gave very poor fits for all gas yields (H_2, C_2, C_3s, C_4s and C_5s). This may be attributable to the larger levels of coke layed down on the catalyst with IPL VTB/VGO. With IPL VGO and DA-300, coke yield was linear in both temperature and C/O ratio while for VTB/VGO it was linear in C/O ratio only. Low root mean square errors for coke yield of 0.27 and 0.65% occur, respectively, with both data sets. Similar behaviour is also observed for the expressions for conversion. The IPL VGO conversion equation

has an extra C/O term but error is 1.29% versus 1.34% for IPL VTB/VGO conversion. Both sets of equations can be used in combination to calculate MAT yields from any combination of these feedstocks.

The effect of conversion on product yields for the IPL VTB/VGO mixture is similar to those experienced for IPL VGO. With increasing conversion, light ends, C_3s, C_4s and coke yields increase while light cycle and decant oil yields decrease. For the VTB/VGO mixture, C_6+ gasoline yield goes through a maximum of 43 wt.% at 72 wt.% conversion, which compares to 45.7 wt.% maximum yield at 70 wt.% conversion for the VGO. Care should be exercised in comparing product yields with conversion since it does not correlate with severity (T and C/O). It should be noted that the VTB/VGO gives a higher conversion at similar severities.

TABLE 7.1

MRT Product Yield Data for IFL VTB in VGO (33.7/66.3) and LA-300

Test	MRT 432	MRT 433	MRT 440	MRT 436	MRT 434	MRT 435	MRT 437	MRT 441	MRT 438	MRT 439	MRT 514	MRT 495	MRT 473	MRT 442
Mass Balance, wt%	95.4	97.3	103.0	98.3	97.3	100.0	100.4	100.6	96.6	102.3	96.9	101.3	105.8	106.5
T, °C	450	450	450	470	471	470	470	471	490	490	490	490	490	490.5
C/O, g/g	3.09	6.14	6.53	2.97	3.05	5.29	6.00	7.54	2.86	5.56	6.37	7.24	8.15	7.39
Yields, wt% FF														
H_2	0.26	0.38	0.42	0.31	0.32	0.45	0.45	0.55	0.37	0.51	0.67	0.48	0.48	0.53
CH_4	0.45	0.56	0.79	0.62	0.79	0.97	0.94	1.30	1.01	1.34	1.77	1.77	1.60	1.91
ΣC_2	1.80	2.37	3.04	2.12	2.64	3.29	3.24	3.97	2.95	4.03	4.98	4.91	4.66	5.28
ΣC_3	4.69	5.53	6.07	5.29	5.24	6.34	7.64	9.63	6.48	7.12	8.21	8.08	7.54	7.91
ΣC_4	9.54	12.0	11.8	9.71	8.32	12.2	14.0	16.1	11.1	13.0	14.4	14.5	14.1	14.1
ΣC_5	5.92	8.86	7.19	3.07	3.67	8.14	4.57	4.27	3.42	8.32	9.45	9.27	9.91	9.26
C_5+ gasoline	45.9	46.4	45.2	43.0	46.9	47.5	43.2	38.2	41.5	45.5	42.5	44.1	42.4	41.7
C_6+ gasoline	40.0	39.5	38.0	39.9	43.2	39.3	38.6	33.9	38.1	37.2	33.1	34.8	32.5	32.4
LCO	21.6	14.7	14.8	21.8	20.9	14.6	14.4	12.9	20.6	14.0	11.7	12.8	11.8	12.2
BO	8.81	4.61	4.97	10.3	7.82	5.04	4.96	4.3	11.5	5.18	4.16	4.42	4.33	3.66
Coke	7.56	12.3	14.2	7.81	8.15	11.0	12.5	14.8	5.84	11.1	14.1	11.2	15.2	15.1
Conversion	69.6	80.7	80.2	67.9	71.9	80.3	80.6	82.8	67.9	80.8	84.2	82.8	83.9	84.1
C_6+ gasoline/Conversion	0.575	0.489	0.474	0.588	0.601	0.489	0.479	0.409	0.561	0.460	0.393	0.420	0.387	0.385
Coke/Conversion	0.109	0.152	0.177	0.115	0.113	0.137	0.155	0.178	0.086	0.137	0.167	0.135	0.181	0.180
C_6+ gasoline/coke	5.28	3.22	2.68	5.11	5.32	3.56	3.09	2.30	6.52	3.36	2.35	3.11	2.14	2.14

FIGURE 7.1

The Effect of C/O Ratio on Conversion for IPL VGO and 33.7% VTB/66.3% VGO with DA-300

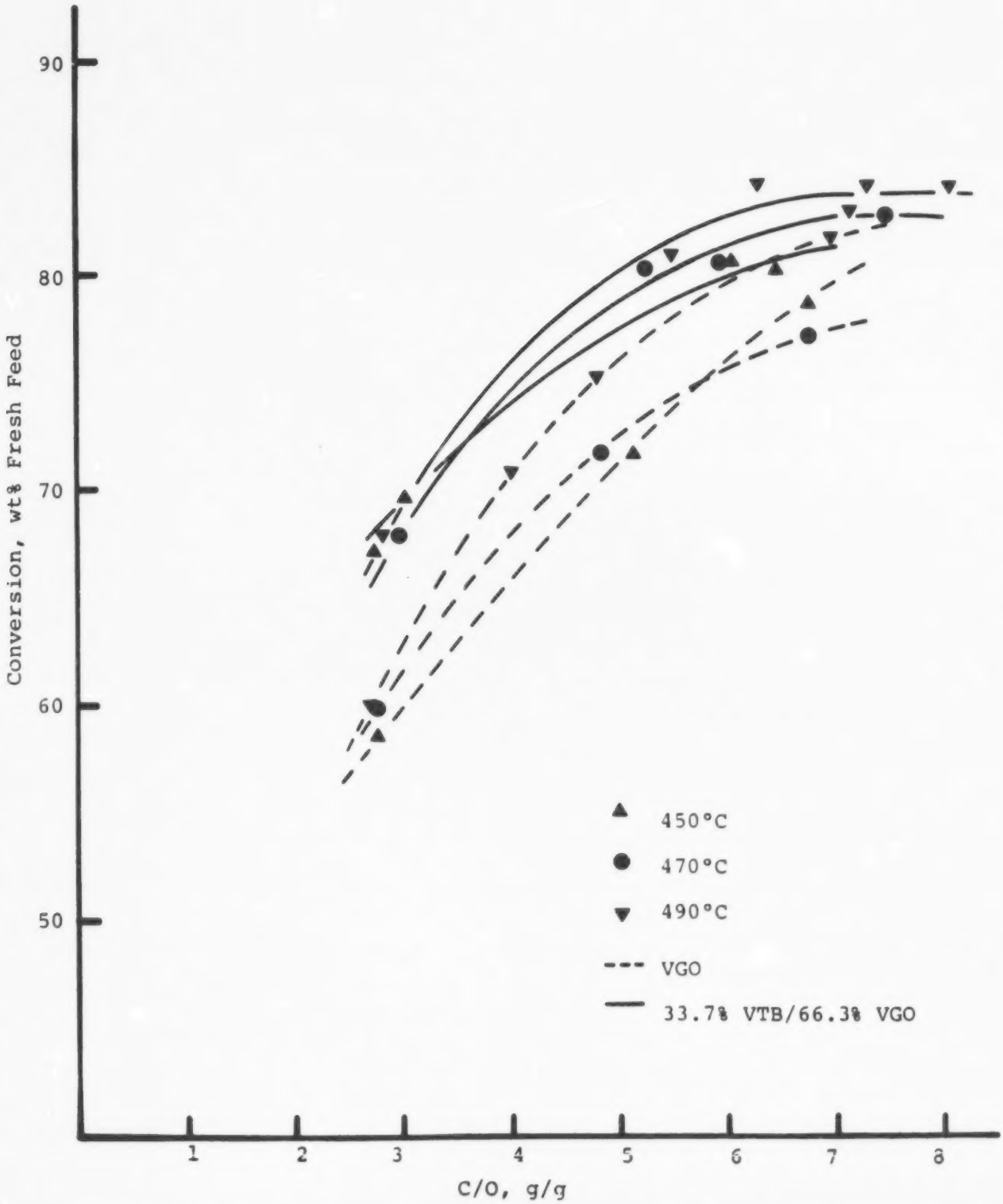


FIGURE 7.2

The Dependence of Coke Yield on C/O Ratio for IPL 33.7% VTB/66.3% VGO and DA-300

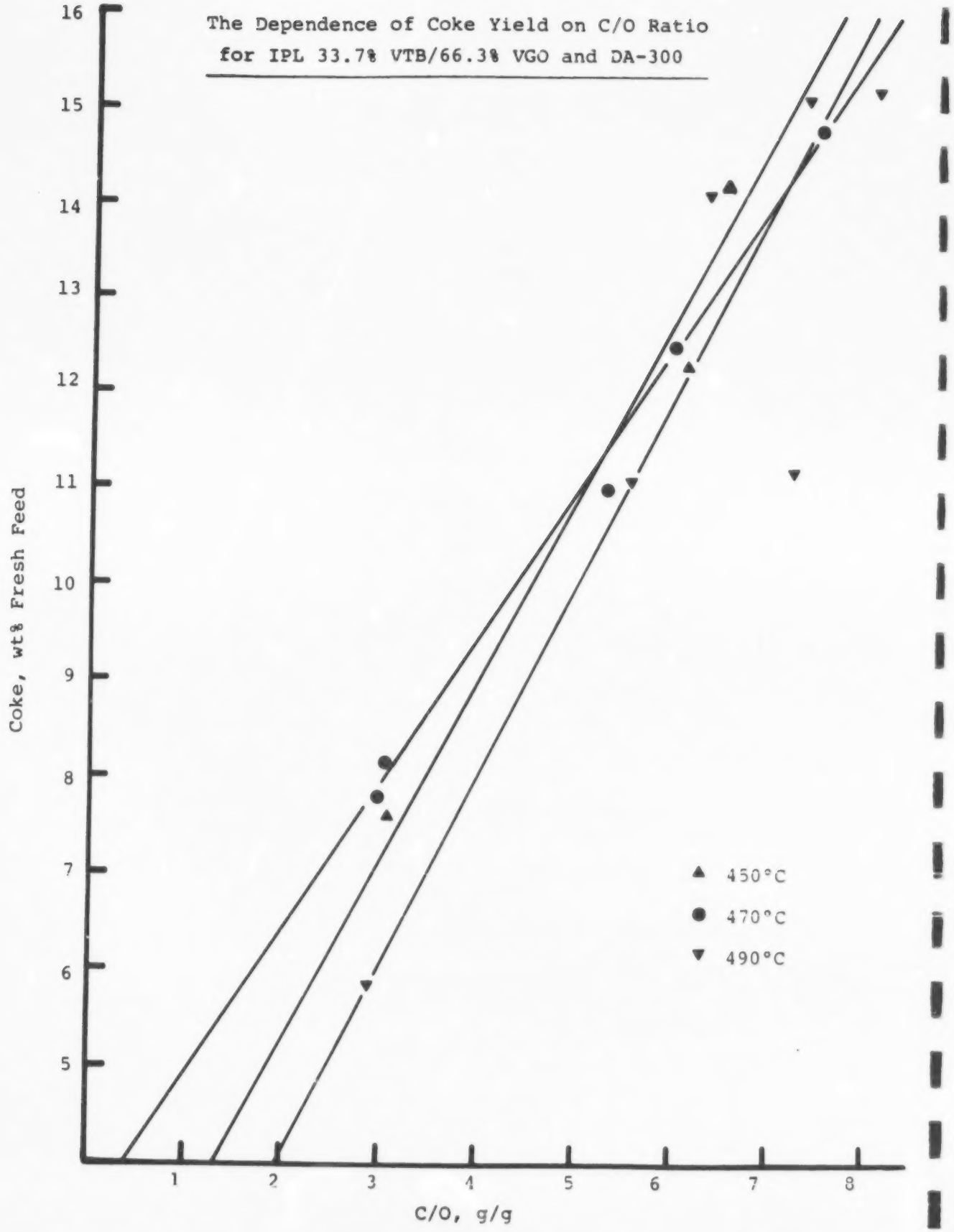
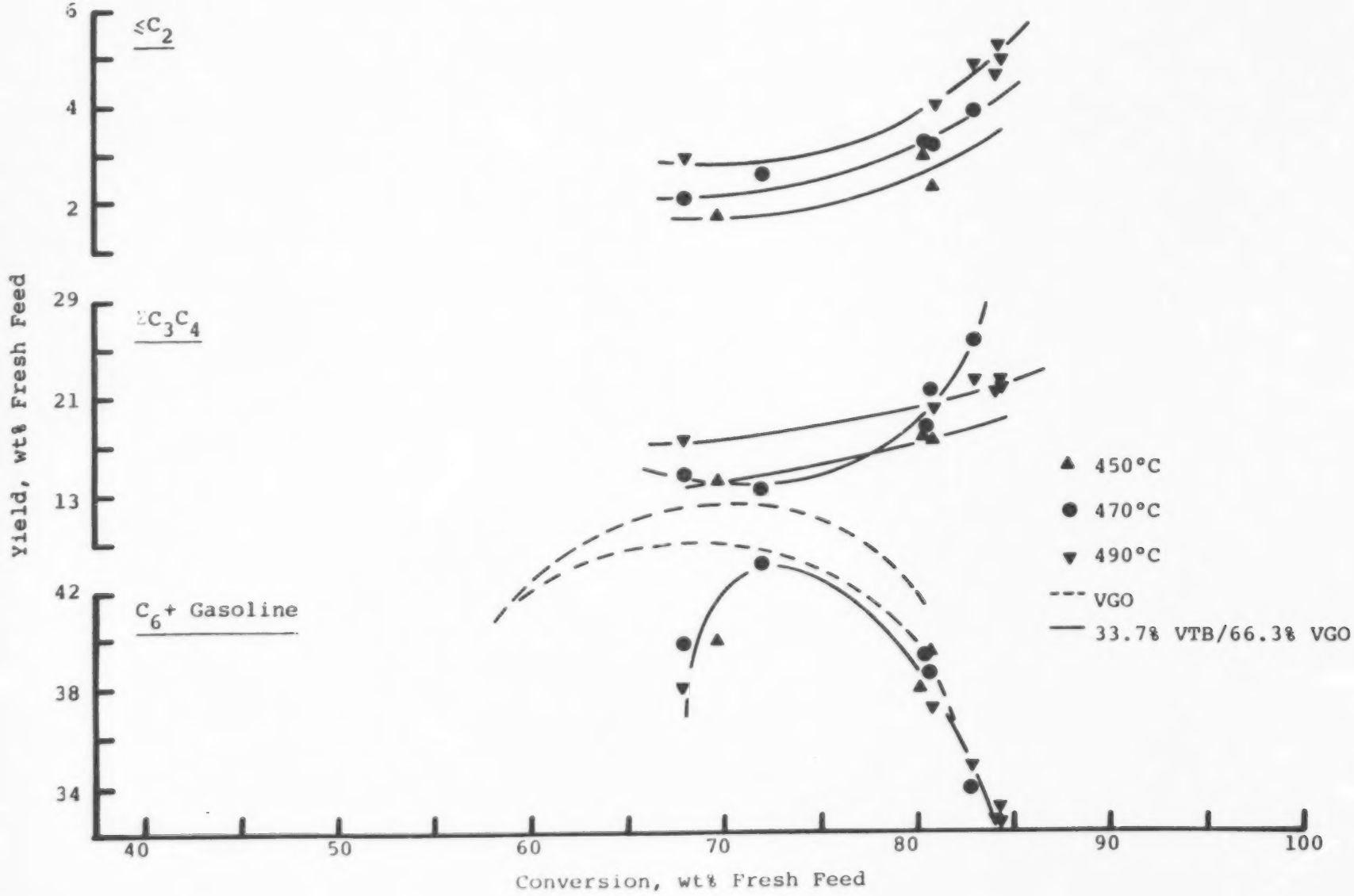


FIGURE 7.3

The Effect of Conversion on MAT Product Yields of IPL 33.7% VTB/66.3% VGO with DA-300



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The Effect of Conversion on MAT Product Yields of IPL 33.7% VTB/66.2% VGO with DA-300

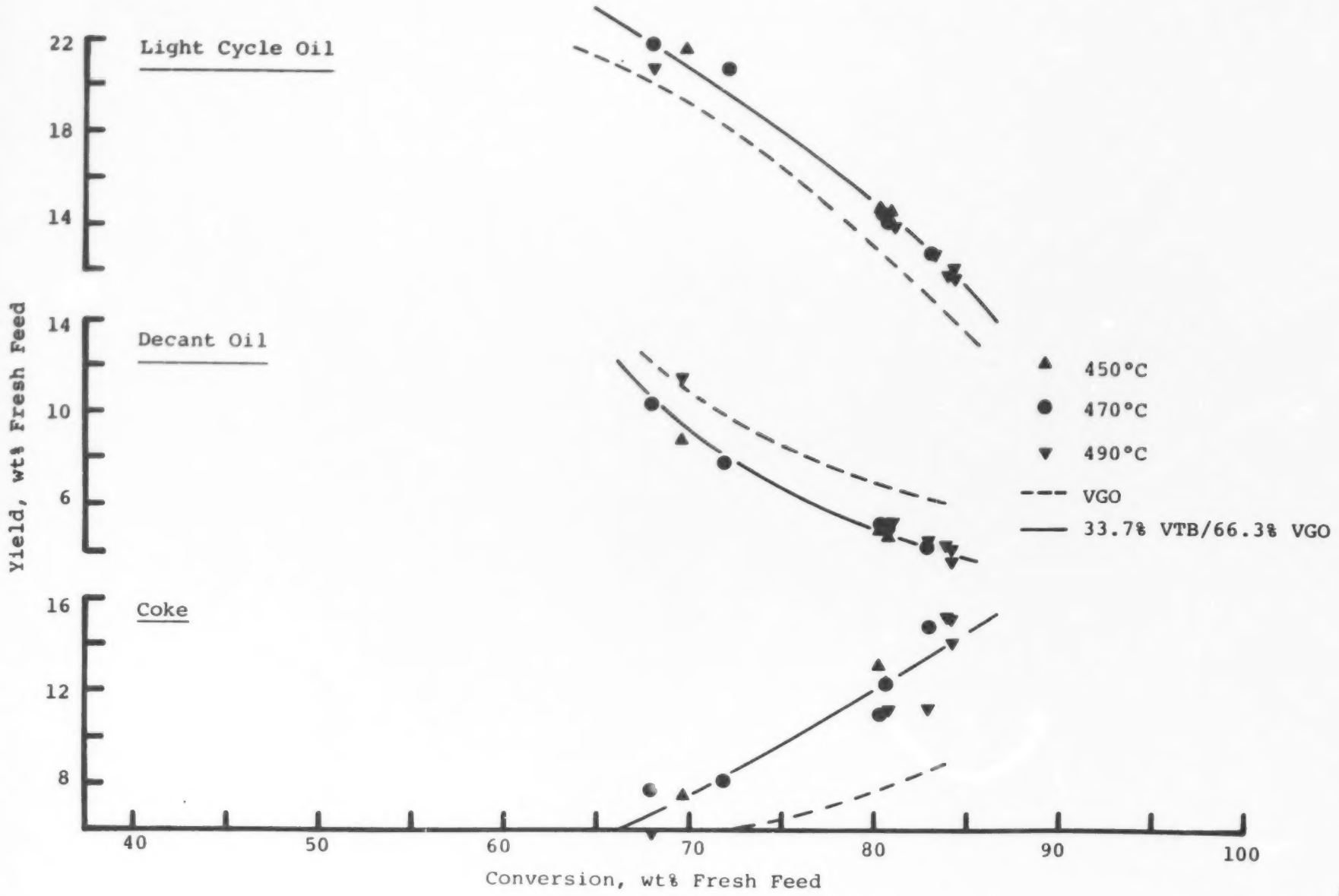


FIGURE 7.4

The Effect of Conversion on MAT Product Ratios of IPL 33.7% VTB/66.3% VGO with DA-300

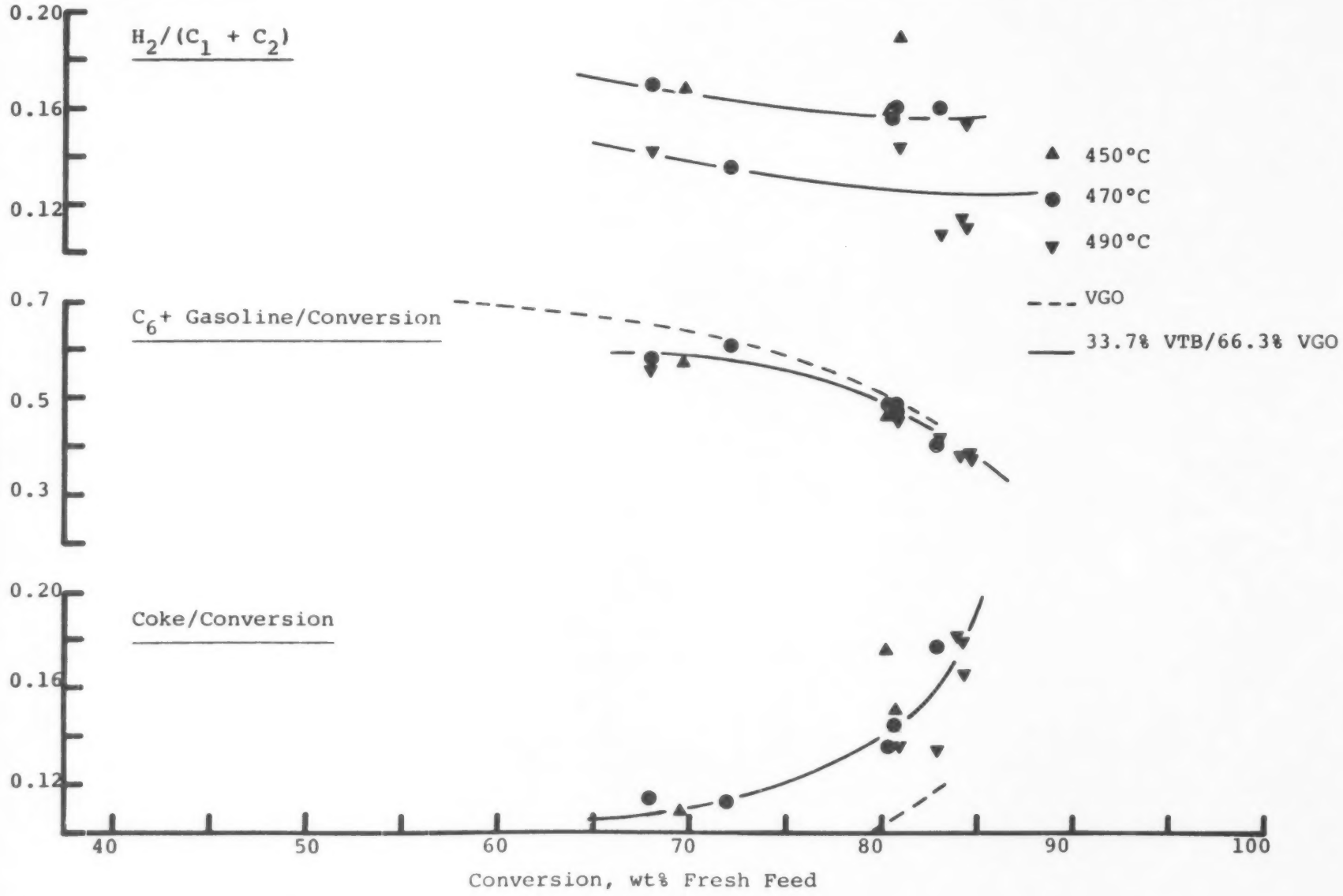


TABLE 7.2

Summary of Regression Analyses for IPL 33.7% VTB/66.3% VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	% Root MSE
H_2	-0.5946		-1.3117	2.7829			0.8066	0.0498
ΣC_2	40.0634			0.0004541		0.00799	0.9584	0.2629
ΣC_3	-15.8219	0.03578	-4.5104			0.0009194	0.6873	0.8569
ΣC_4	169.9126					0.03173	0.8050	1.0734
ΣC_5	1374.8549	-5.8702		0.0005736	0.006194		0.8077	1.2758
C_6+ gaso.	-529.52555		15.4582			-0.1044	0.9407	0.8775
LCO	46.3004			0.003721	-0.0003221	-0.01562	0.9935	0.3509
DO	15.1501			-0.003516	0.0003123	0.008307	0.9927	0.2463

Coke Yield (wt.%) = 2.11 + 1.721 (C/O) — R^2 = 0.9626, Root MSE = 0.65

Conversion (wt.%) = -47.13 + 9.192 (C/O) - 0.5899 $(C/O)^2$ — R^2 = 0.9632, Root MSE = 1.34

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

8) EFFECT OF LLOYDMINSTER ATB ON MAT PRODUCT YIELDS

The vacuum distillation of Lloydminster ATB showed that the material readily cracked before typical 504°C+ residua could be produced. As a result, Lloydminster ATB was chosen for this residuum evaluation. The ATB contains 38.9 v.% (37.0 wt.%) VGO in 504+ VTB. Successive amounts of Lloydminster ATB were added to Lloydminster VGO to produce feedstocks for MAT evaluations. The most concentrated feed contained 41.5 wt.% ATB and had a Conradson carbon residue of 7.2 wt.%, which is similar to that of the IPL VTB/VGO mixture evaluated. On a VTB basis, however, the Lloydminster blend contains only 26.1 wt.% VTB versus 33.7 wt.% for the IPL blend. This is indicative of the "heaviness" of Lloydminster VTB. MAT experiments were conducted at 490°C and a C/O ratio of approximately four with DA-300. Experimental variables and product yields for each of these tests are listed in Table 8.1 and the product yields are presented graphically as a function of ATB content in the feedstock (Figure 8.1).

Yield data indicate Lloydminster ATB has a similar effect on cracking yields as IPL VTB for some but not all of the products. For 0 to 41.5 wt.% additions of ATB (or 0-26.1 wt.% VTB), product yields for hydrogen, methane, light ends, C_3s, C_4s and C_5s as well as coke were observed to increase 46.4, 135, 79, 31, 20.5, 26.1 and 69% in relative terms. All gas yield increases in relative terms were similar to those observed for IPL VTB. The increase in coke yield (69%), however, is much less than the increase experienced with IPL VTB/VGO (93%). This is not consistent with either the Conradson carbon level of the mixtures, which are similar, nor with the level of DO + coke precursors, which are much greater for the Lloydminster material. With Lloydminster feeds C_6+ gasoline yields decrease from 41.3 wt.% to 35.8 wt.% for additions of 41.5 wt.% ATB. Light cycle oil yields are reasonably constant throughout the range of ATB additions but decant oil yields decrease some 2 wt.% in absolute terms. This is compensated for by an equivalent increase in coke yield. Therefore, for Lloydminster ATB we have the anomally of adding more decant oil and oil precursors to feeds without forming more of these products when they are cracked.

Data in Table 8.1 can also be used to calculate either ATB or VTB yields. Results of such calculations for ATB are listed in Table 8.2 and, when experimental noise is considered, the range of yields anticipated for ATB at 490°C and C/O=4 with this sample of DA-300 can be determined. A comparison of Lloydminster VGO and ATB yields (Table 8.2) shows that gas yields increase dramatically. Hydrogen yield increases from 0.28 to 0.62 wt.%, methane from 0.40 to 1.68 wt.% and total light ends from 2.48 to 7.39 wt.%. LPGs also increase but not to the same extent, C_3s increase from 4.2 to ~7.8 wt.%, while C_4s increase from 7.5 to 11.5 wt.%. Coke yield increases from 3.36 to 9.5 wt.% which is a 2.83 fold increase and is less than the 3.78 fold increase experienced with IPL VGO. Lloydminster ATB does produce significantly less decant oil (7.5 vs 15.1) but more cycle oil (25 vs 21.7) than its vacuum gas oil. The larger yield of light cycle oil is consistent with a larger LCO precursor level in the ATB. Overall total liquid product yield from Lloydminster ATB appears to be nearly as great as that of the VGO (77 vs 81.7). While this is encouraging, other factors such as catalyst addition rates must be considered if such processing is to become economically viable, since this ATB contains high levels of Ni and V.

TABLE 8.1

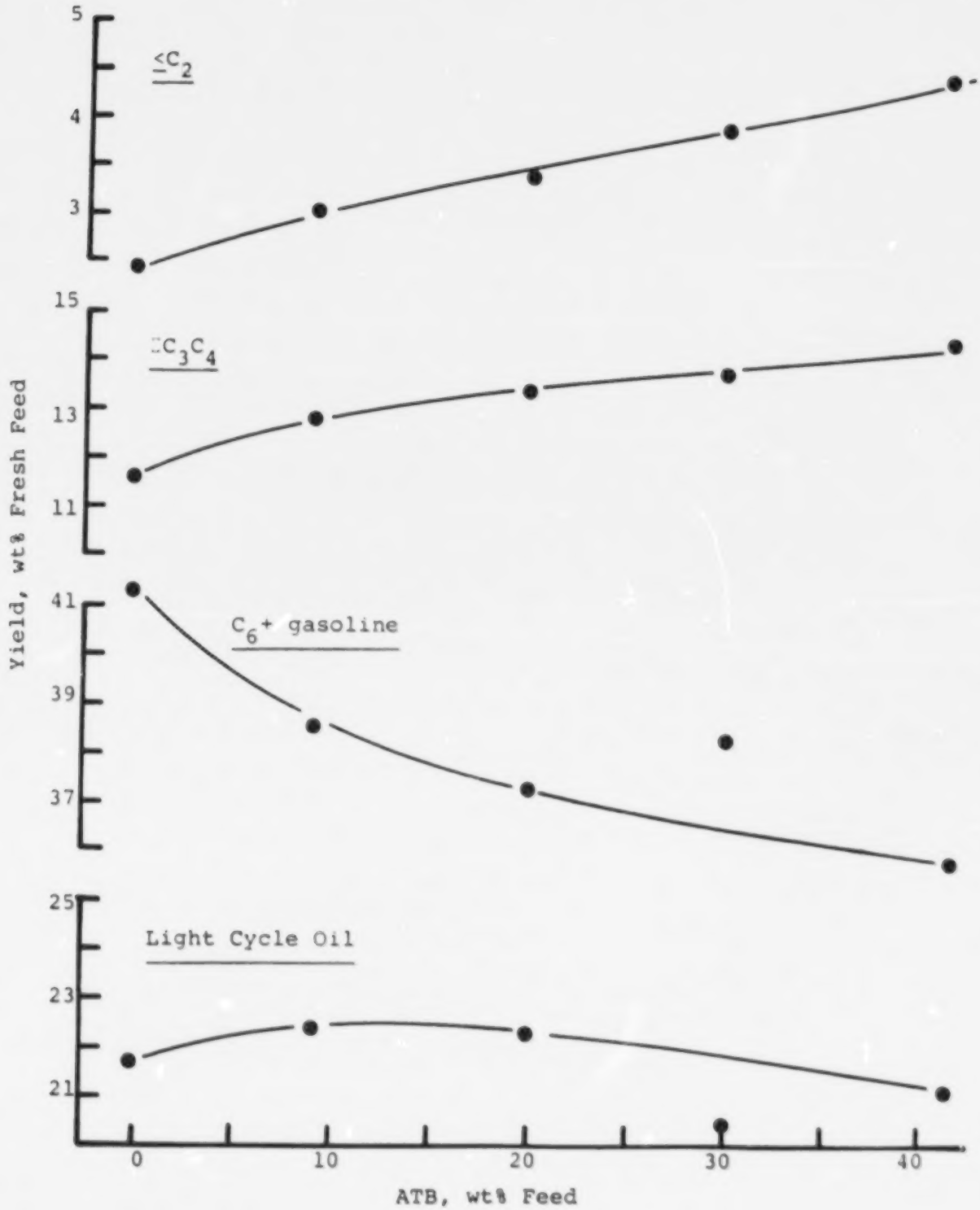
MAT Product Yields for Lloydminster ATB/VGO Mixtures & DA-300

Test	MAT 389	MAT 390	MAT 391	MAT 392	MAT 393
Mass Balance, wt%	103.2	103.5	103.2	101.8	99.7
T, °C	490	490	490	491	491
C/O, g/g	3.66	4.17	3.64	3.88	4.25
Feed Composition, wt%					
ATB	0	9.1	20.0	30.0	41.5
VGO	100	90.9	80.0	70.0	58.5
VTB	0	5.73	12.6	18.9	26.1
Product Yields, wt%					
H_2	0.28	0.31	0.36	0.38	0.41
CH_4	0.40	0.53	0.62	0.78	0.94
C_2	2.48	3.01	3.39	3.89	4.44
C_3	4.16	4.57	4.93	5.09	5.45
C_4	7.45	8.18	8.24	8.69	8.98
C_5	4.40	5.37	5.45	5.88	5.55
C_5+ gasoline	45.7	43.8	42.7	44.2	41.3
C_6+ gasoline	41.3	38.5	37.3	38.3	35.8
LCO	21.7	22.4	22.3	20.5	21.1
DO	15.1	13.7	13.7	12.5	13.0
Coke	3.36	4.25	4.72	5.11	5.68
Conversion	63.2	63.9	64.0	67.0	65.9
C_6+ gasoline/Conversion	0.653	0.603	0.583	0.572	0.543
Coke/Conversion	0.0532	0.0665	0.0738	0.0763	0.0862
C_6+ gasoline/coke	12.3	9.07	7.90	7.50	6.30

FIGURE 8.1

The Effect of ATB on MAT Product Yields for Lloydminster ATB/VGO Mixtures and DA-300

C/O = 4, T = 490°C



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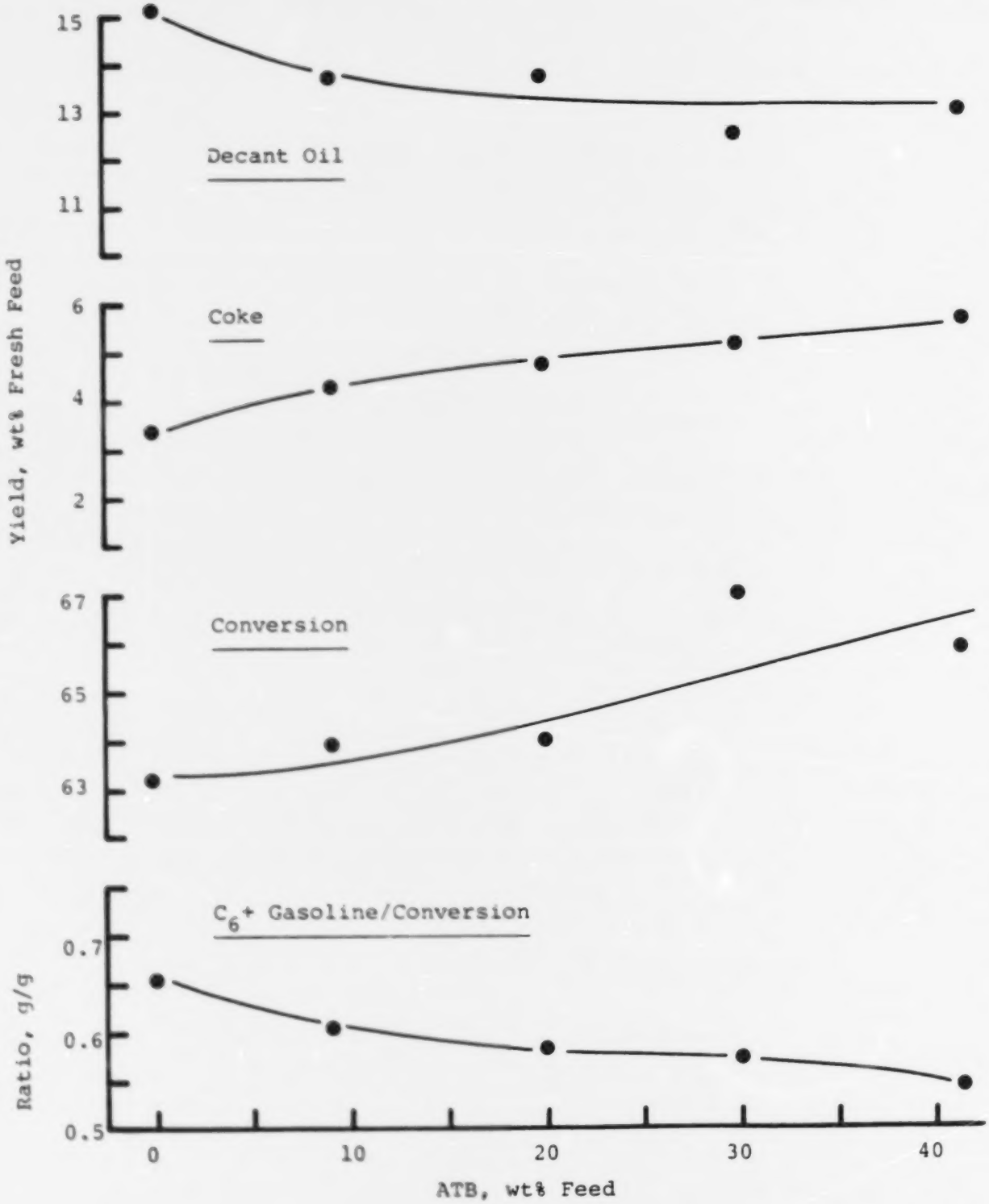
The Effect of ATB on MAT Product Yields for Lloydminster ATB/VGO Mixtures and DA-300

C/O = 4, T = 490°C



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The Effect of ATB on MAT Product Yields for Lloydminster ATB/VGO Mixtures and DA-300

C/O ≈4, T = 490°C

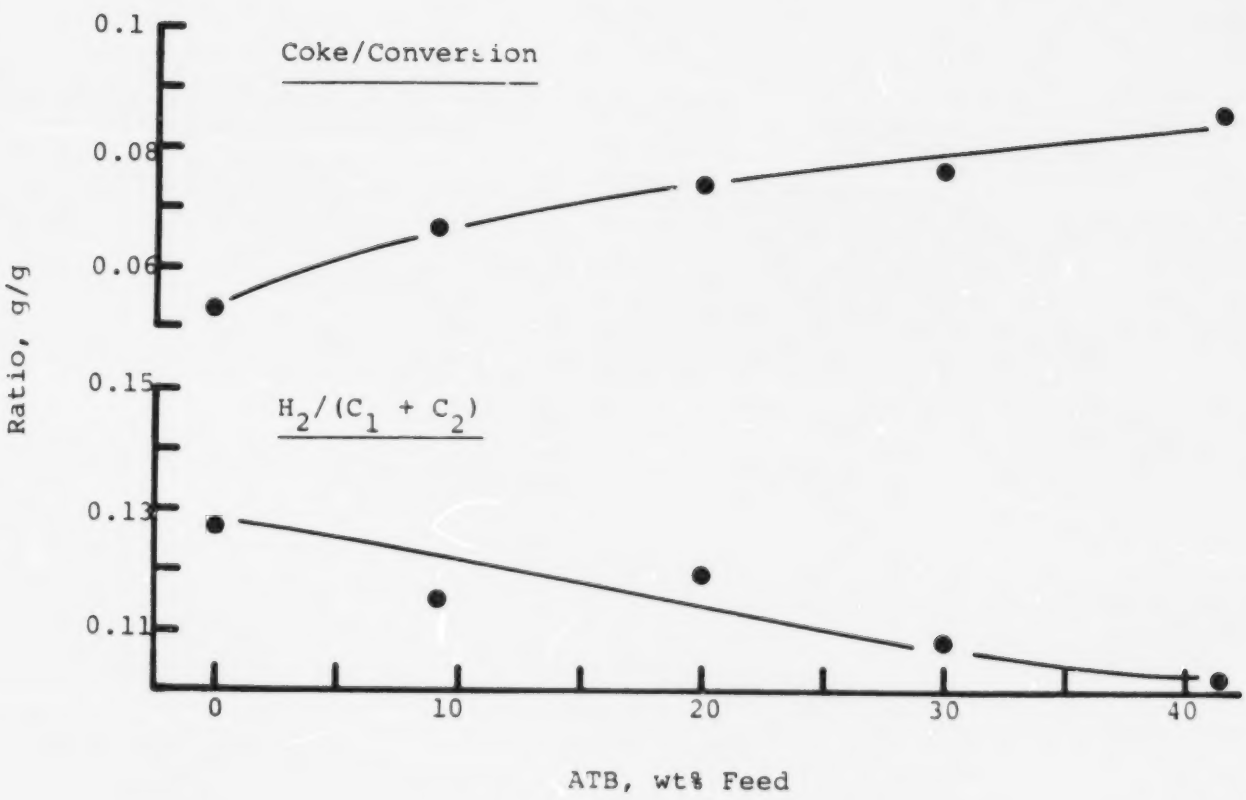


TABLE 8.2

Calculated Lloydminster ATB product Yields with DA-300*
(T=490°C, C/O ≈4)

Material	VTB					VGO
Test	MAT 390	MAT 391	MAT 392	MAT 393	Average+	MAT 389
Wt% ATB in Feed	9.1	20.0	30.0	41.5		0
Product Yields, wt%						
H_2	0.61	0.68	0.61	0.59	0.62	0.28
CH_4	1.83	1.50	1.67	1.70	1.68	0.40
ΣC_2	8.30	7.03	7.03	7.18	7.39	2.48
ΣC_3	8.67	8.01	8.01	7.26	7.99	4.16
ΣC_4	15.5	11.4	11.4	11.6	12.5	7.45
ΣC_5	15.1	9.65	9.65	9.33	10.9	4.40
C_5+ gasoline	24.8	30.7	30.7	40.7	31.7	45.7
C_6+ gasoline	10.5	21.3	21.3	31.3	21.1	41.3
LCO	29.4	24.7	24.7	17.7	24.1	21.7
DO	0.28	8.1	8.1	6.43	5.72	15.1
Coke	13.1	10.2	9.19	8.95	10.4	3.36

*Calculated from the weight averaged composition
+Average of MAT 390, MAT 391, MAT 392 and MAT 393 ATB Product Yields

9) MAT PRODUCT YIELD DATA FOR LLOYDMINSTER 41.5 wt.% ATB/ 58.5 wt.% VGO AND DA-300

The mixture of 41.5 wt.% Lloydminster ATB in 58.5 wt.% Lloydminster VGO was cracked with DA-300 catalyst at 3 C/O ratios for each of three temperatures. This data was developed in order to establish the effect of ATB on product yields for the range of temperatures and C/O ratios studied with Lloydminster VGO. Experimental conditions and corresponding MAT product yields are found in Table 9.1.

The effect of C/O ratio on Lloydminster ATB/VGO mixture's conversion is shown graphically in Figure 9.1. Feedstock containing 41.5 wt.% ATB has a greater conversion (7-12 wt.%) than the corresponding VGO at the same C/O ratio. The response of conversion to C/O ratio is also different for the Lloydminster ATB/VGO feed than for VGO itself. The former material's conversion is very responsive to changes in C/O ratio for $2 \leq C/O \leq 4$ but for $C/O > 5$ conversion approaches an upper limit of 83 wt.%. For VGO at $C/O > 3$, however, there is a smaller but steady response of conversion to increasing C/O ratio. A limiting conversion is approached for VGO only for $C/O > 7$. The Lloydminster ATB/VGO mixture's conversion is much less affected by temperature (1-2% increase from 450 to 490°C) than the conversion of VGO, which increases approximately 3% for a 450 to 490°C increase in reaction temperature.

The relationship between coke yield and C/O ratio for the MAT experiments with 41.5 wt.% Lloydminster ATB in VGO (Figure 9.2) is as follows:

coke, wt.% = 1.935 (C/O) + 0.922 T = 450°C
coke, wt.% = 1.570 (C/O) + 0.543 T = 470°C
coke, wt.% = 1.530 (C/O) + 0.373 T = 490°C

These expressions can be compared with those derived for Lloydminster VGO and DA-300:

coke, wt.% = 1.022 (C/O) - 0.127 T = 450°C
coke, wt.% = 0.968 (C/O) + 0.084 T = 470°C
coke, wt.% = 1.091 (C/O) - 1.022 T = 490°C

The C/O coefficient for the 450°C ATB coke yield equation, 1.935, seems large with respect to the coefficients (1.570 and 1.530) at other temperatures. The coke yield-C/O data at that temperature is linear, quite distinct and may be due to adsorption of uncracked high molecular weight species. Nevertheless, coke selectivity for Lloydminster ATB/VGO is 1.5 times greater than that for the VGO, which confirms that the former material has a greater coke-forming ability. The intercepts of the coke-C/O relationships for the ATB/VGO mixture are all larger than those from the VGO expressions. This again is another indication of the greater coking propensity of the ATB/VGO blend.

Product yields for the 41.5 wt.% Lloydminster ATB/58.5 wt.% Lloydminster VGO mixture are shown in Figure 9.3 as functions of conversion. Light ends yields for the mixture are greater than those for the VGO until conversions of 72-73 wt.% are achieved, at which point these yields become similar for both feedstocks. C_3 and C_4 yields also behave in a similar fashion for Lloydminster ATB/VGO and VGO feeds. The ATB/VGO mixture gives a maximum C_6+ gasoline yield of 37.3 wt.% at 70.5 wt.% conversion, which is only slightly less than the VGO maximum C_6+ gasoline yield of 38.6 wt.% which occurs at 64 wt.% conversion. The 1.3 wt.% reduction in C_6+ gasoline for Lloydminster ATB/VGO versus Lloydminster VGO is less than the 2.7 wt.% reduction observed for IPL VTB/VGO and IPL VGO. Light cycle oil yields for the Lloydminster ATB/VGO mixture are from 0 to 2 wt.% absolute greater than those for Lloydminster VGO for conversions. Up to 57.5 wt.% conversion, LCO yields are similar for both feeds; however, with increasing conversion the LCO yields for the ATB/VGO mixture decline less rapidly than those of the VGO. Decant oil yields for both Lloydminster ATB/VGO and VGO are similar except for conversions greater than 65 wt.%, where the former material yields successively less decant oil than the latter material.

A summary of regression analyses for Lloydminster ATB/VGO MAT product yields are listed in Table 9.2. As observed with IPL residua, some yields give very poor fits, particularly C_4s, C_5s and C_6+ gasoline. Coke yields for both Lloydminster ATB,VGO and VGO (Table 5.4) are linear in both temperature and C/O. The former regression gives rise to larger coefficients for the constant and C/O terms and a smaller value for

the temperature term. This could be interpreted as greater and less temperature dependent coking propensity for the ATB/VGO regressions but even so all are equivalent or less than experimental error.

Both IPL and Lloydminster residua have produced more gases and coke and less gasoline than their corresponding gas oils. Light ends products ($\leq C_2$) are typically used as fuel gas in a refinery and their production should, if possible, be minimized. The ratio of hydrogen to hydrocarbons ($H_2/(C_1+C_2)$) in the light ends is an indication of the relative amounts of hydrogen elimination and methyl and ethyl group cleavage. For all feedstocks, higher conversions favour the former reactions over the latter reactions (Figure 9.4). With residua, more cleavage reactions occur than hydrogen elimination reactions since the ratio of $H_2/(C_1+C_2)$ is lower than that for VGOs. This is fortunate since residua are hydrogen deficient to begin with. Note, however, in absolute terms residua produce more hydrogen and C_2 hydrocarbons than vacuum gas oils. Residua also yield greater amounts of C_3 and C_4 hydrocarbons, which under certain conditions can be advantageous since these materials can be processed into high octane blending components [9]. The increased coke yield of residua presents a more difficult problem. Since this product is burnt in the FCCU, processing equipment must be sized to accomplish this and withstand the higher regenerator temperatures produced, or reductions in capacity, if possible, must be considered.

TABLE 9.1

MAT Product Yield Data for Lloydminster ATB in VGO (41.5/58.5) and DA-300

Test	MAT 453	MAT 456	MAT 459	MAT 496	MAT 515	MAT 454	MAT 457	MAT 497	MAT 516	MAT 460	MAT 455	MAT 498	MAT 517	MAT 458	MAT461
Mass Balance, wt%	94.5	101.0	98.4	103.0	100.0	95.5	97.1	98.5	99.6	99.1	95.1	93.7	98.8	98.3	98.7
T, °C	449	450	451	451	450	470	470	471	470	470	490	489	490	491	489
C/O, g/g	1.81	3.95	5.42	6.65	7.35	2.48	3.85	4.84	4.93	6.66	1.86	2.61	3.15	5.34	6.91
Yields, wt% FF															
H_2	0.17	0.34	0.44	0.44	0.43	0.23	0.36	0.45	0.39	0.55	0.24	0.32	0.29	0.46	0.64
CH_4	0.40	0.67	0.62	0.67	0.63	0.62	0.72	0.85	0.74	0.95	0.73	0.85	0.81	1.07	1.42
ΣC_2	3.06	3.81	4.22	3.79	3.77	3.43	4.08	4.50	4.08	4.98	3.76	4.20	3.83	5.03	6.02
ΣC_3	4.16	5.78	5.16	5.26	6.44	5.29	6.19	5.57	5.08	7.62	4.40	6.46	6.04	7.73	8.57
ΣC_4	7.13	10.2	10.0	10.5	12.5	9.66	10.9	10.4	8.68	13.8	8.79	11.3	10.8	13.3	14.4
ΣC_5	2.54	3.18	6.28	6.81	4.07	3.63	3.41	6.60	4.59	4.64	3.93	3.91	3.79	4.69	4.85
C_5+ gasoline	34.0	39.6	43.1	41.8	38.3	36.2	40.6	43.5	44.3	39.1	34.4	38.9	40.5	38.2	36.2
C_6+ gasoline	31.5	36.4	36.8	35.0	34.2	32.6	37.2	36.9	39.7	34.4	30.4	35.0	36.8	33.5	31.3
LCO	24.1	22.7	18.8	18.8	18.6	23.2	21.3	19.8	19.3	16.8	23.3	21.5	21.7	18.6	16.6
DO	23.1	9.40	7.33	7.15	6.19	17.8	10.1	7.97	7.88	6.9	22.0	13.3	12.1	8.81	6.63
Coke	4.37	8.56	11.4	12.7	14.2	4.27	6.82	8.32	10.7	10.8	3.36	4.38	5.06	8.31	11.5
Conversion	52.8	67.9	73.9	74.1	75.2	58.9	68.6	72.3	72.8	76.3	54.7	65.2	66.2	72.6	76.7
C_6+ gasoline/Conversion	0.597	0.536	0.498	0.472	0.455	0.553	0.542	0.510	0.545	0.451	0.556	0.537	0.556	0.461	0.408
Coke/Conversion	0.083	0.126	0.154	0.171	0.189	0.072	0.099	0.115	0.147	0.142	0.061	0.067	0.076	0.114	0.150
C_6+ gasoline/coke	7.19	4.25	3.23	2.76	2.41	7.68	5.47	4.43	3.71	3.18	9.11	8.01	7.32	4.04	2.72

FIGURE 9.1

The Effect of C/O Ratio on Conversion for Lloydminster VGO and 41.5% ATB/58.5% VGO with DA-300

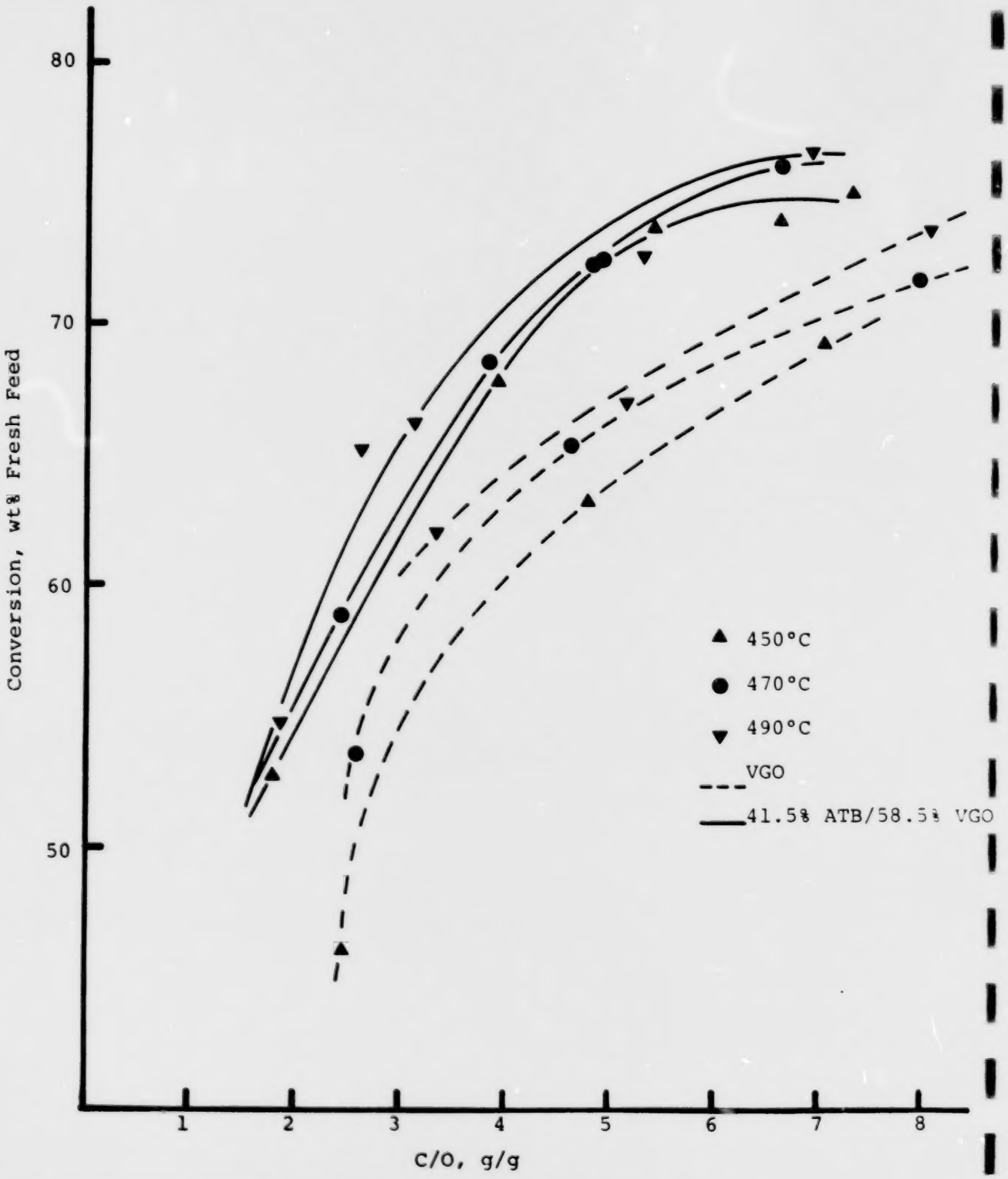


FIGURE 9.2

The Dependence of Coke Yield on C/O Ratio for Lloydminster 41.5% ATB/58.5% VGO and DA-300

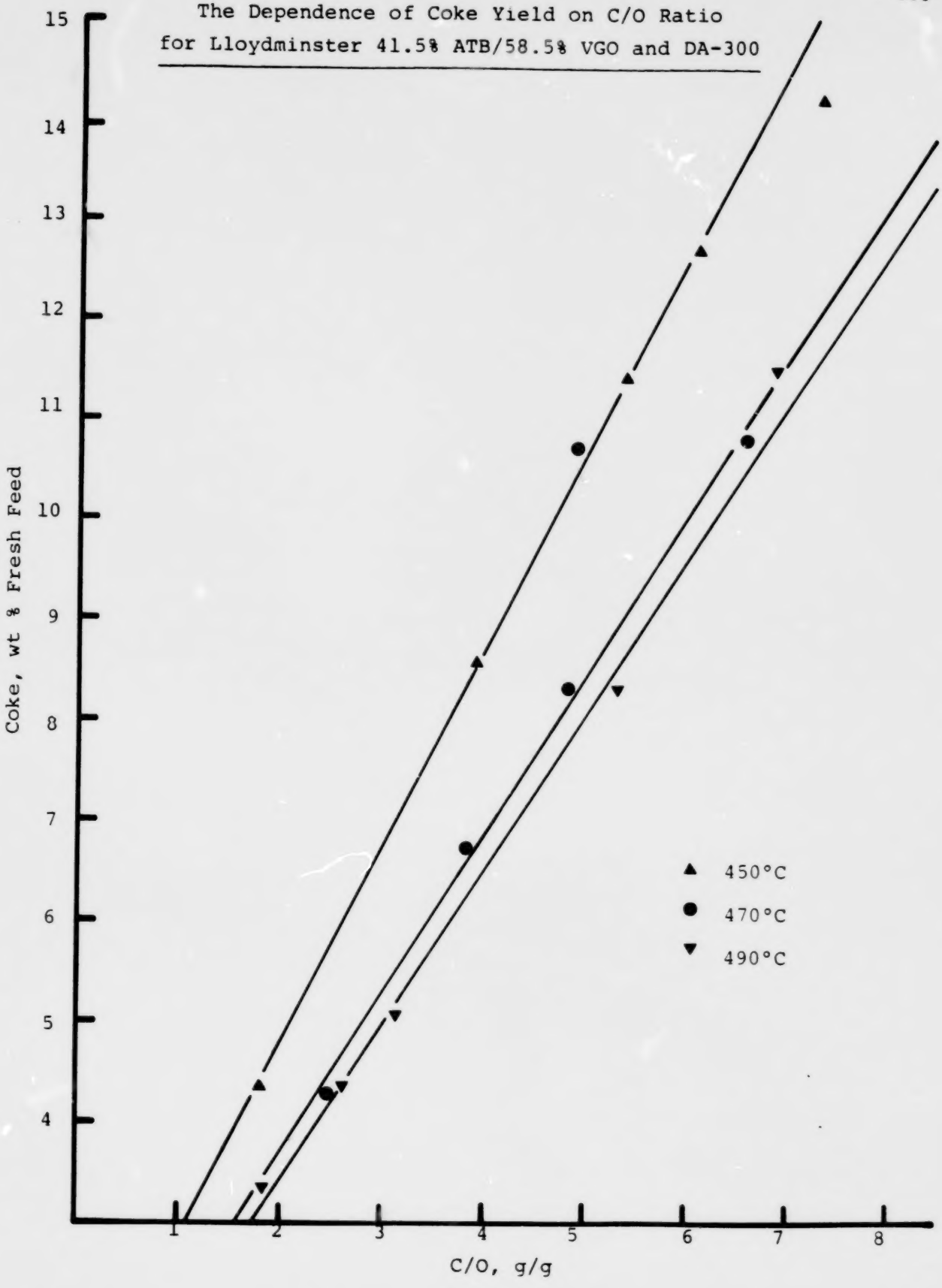


FIGURE 9.3

The Effect of Conversion on MAT Product Yields of Lloydminster 41.5% ATB/58.5% VGO with DA-300

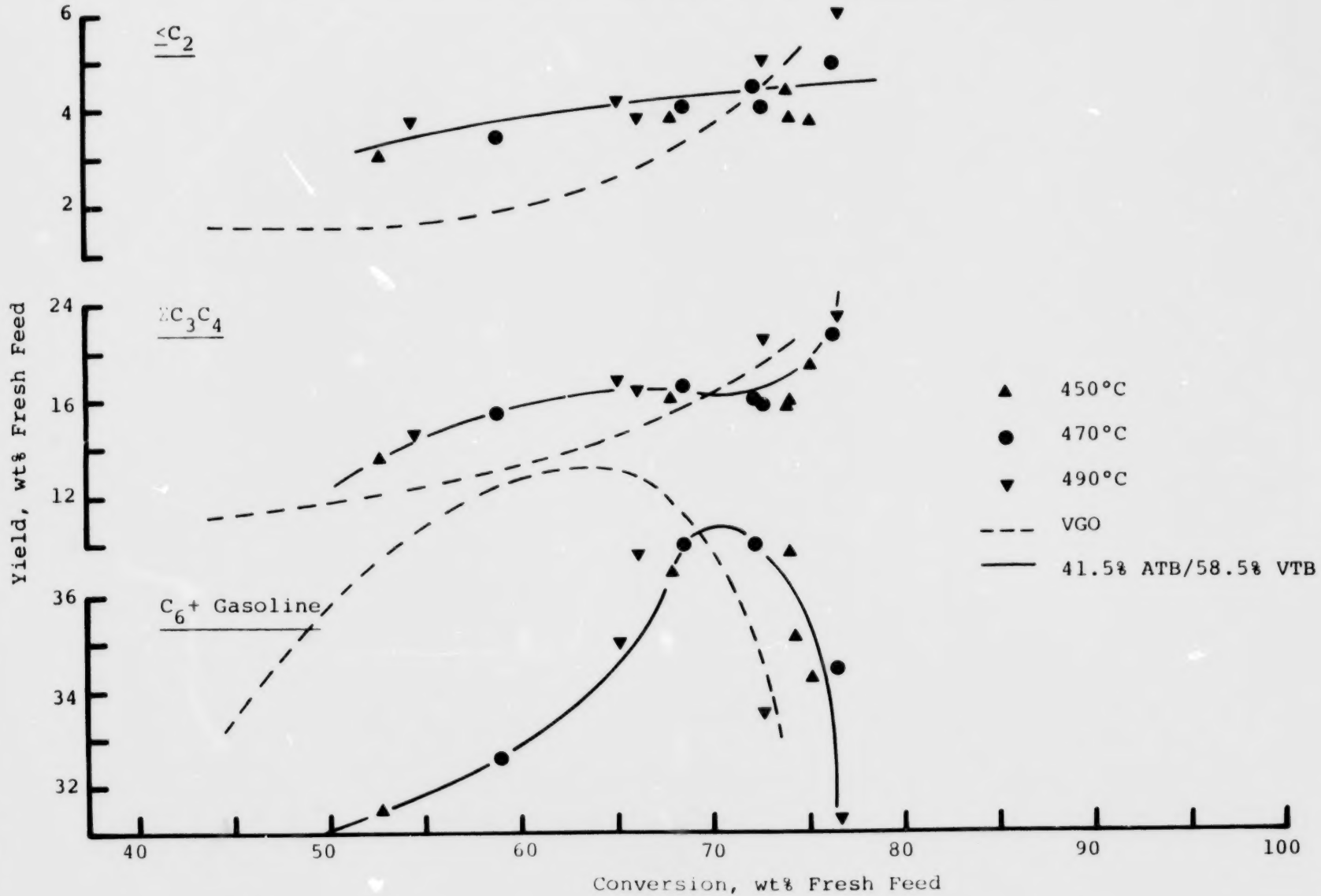


FIGURE 9.4

The Effect of Conversion on MAT Product Yields for Lloydminster 41.5% ATB/58.5% VGO with DA-300

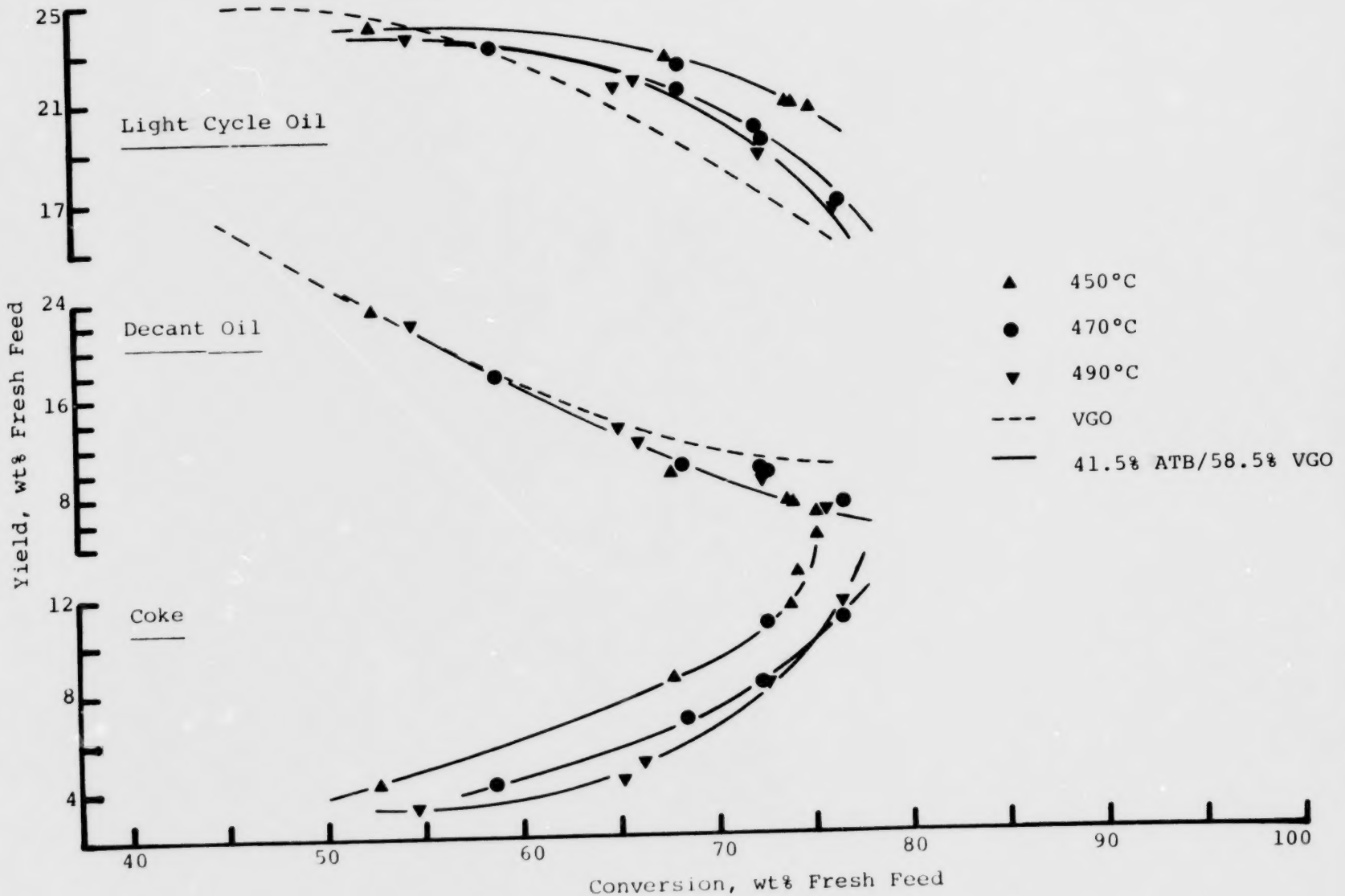


FIGURE 9.5

The Effect of Conversion on MAT Product Ratios of Lloydminster 41.5% ATB/58.5% VGO with DA-300

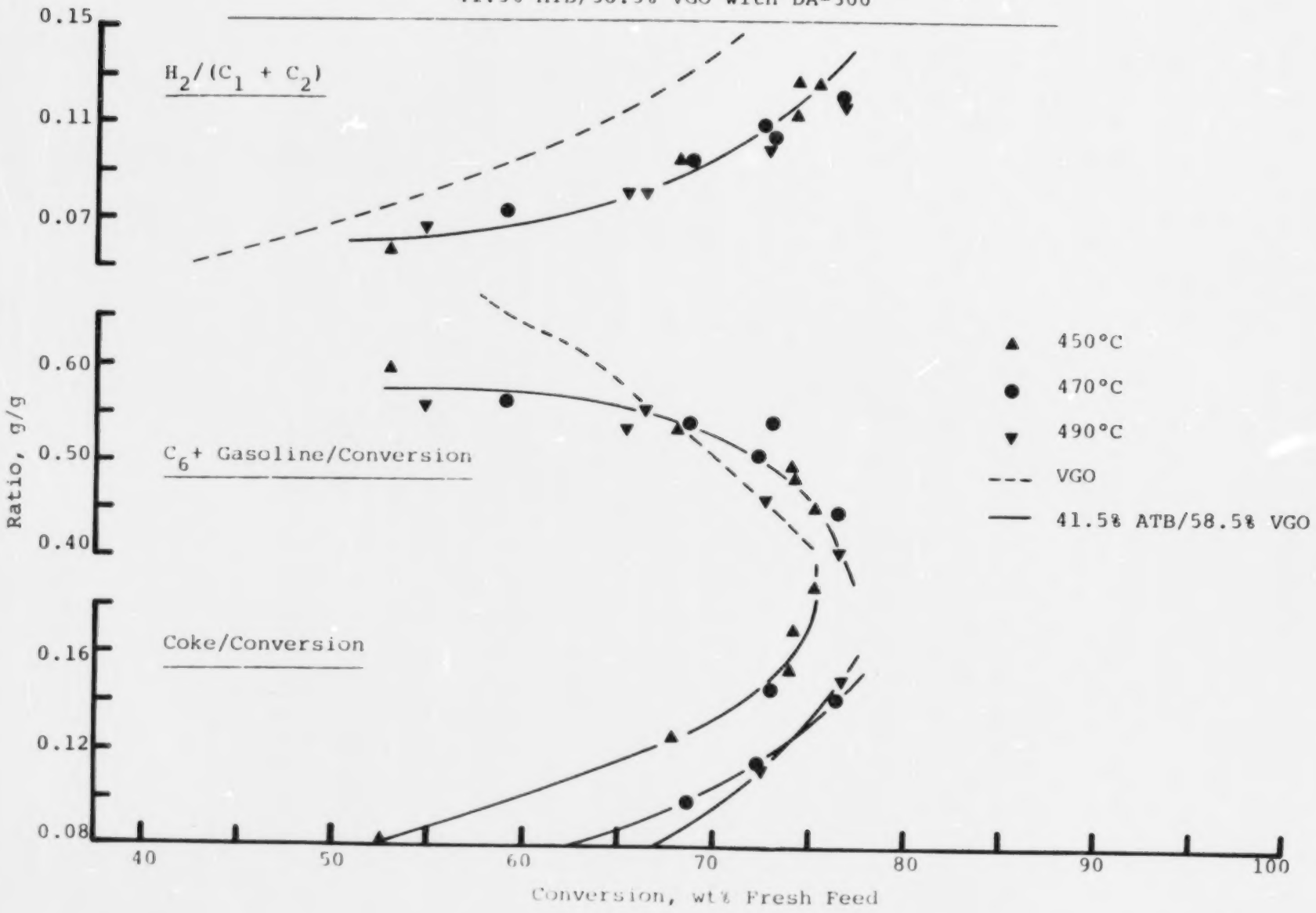


TABLE 9.2

Summary of Regression Analyses for Lloydminster 41.5% ATB/58.5% VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + f(CON^2)$

Component	a	b	c	d	e	f	R^2	% Root MSE
H_2	2.4988		-0.09548	2.6217E-05		0.0007541	0.9462	0.0326
C_2	17.8391		-0.6942	0.0004032		0.004402	0.8623	0.3053
C_3	72.4677	-0.1282	-1.2365	0.002876			0.7507	0.6972
C_4	-8.1275				5.3528E-05	0.001495	0.6846	1.2122
C_5	0.7382					0.0007832	0.3935	1.0124
C_6+ gaso.	-107.96885		4.6545		-5.2895E-05	-0.03462	0.6634	1.6992
LCO	-16.6215	-0.02928	1.9132			-0.01692	0.9836	0.3442
DO	116.3852	0.02865	-2.8979			0.01681	0.9970	0.3434

Coke Yield (wt.%) = 23.90 + 1.672 (C/O) - 0.04923T — R^2 = 0.9650, Root MSE = 0.70

Conversion (wt.%) = 36.331 + 11.766 (C/O) - 0.8837 $(C/O)^2$ — R^2 = 0.9605, Root MSE = 1.65

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

10) THE EFFECTS OF Ni/V CONTAMINATION ON DA-300

Metals present in crude oil and its residua (nickel and vanaxium) are known to destroy fluid catalytic cracking catalyst activity. This contamination problem is alleviated by constantly removing equilibrium catalyst from the unit and replacing it with fresh high activity catalyst. The makeup rate for such additions can be expresed by the following relationship:

$$\text{Catalyst Addition } (kg/m^3 \text{ of feed}) = \rho_{FF}\ (kg/m^3) \times \frac{\text{Ni Equivalents in Feed } (\mu g/g)}{\text{Ni Equivalents on Equilibrium Catalyst } (\mu g/g)}$$

ρ_{FF} density of fresh feed.

The addition rate of catalyst is proportional to the amount of metallic impurities in the feed and inversely proportional to the amount of impurities a catalyst will tolerate to maintain a given activity. Therefore, for feeds such as residua which contain high levels of impurities, large levels of these metals must be tolerated by the catalyst in order to maintain a reasonable rate of addition. This addition rate also represents a major processing cost in terms of catalyst consumption rates and should be as low as possible.

In order to establish the effect of metals on these catalysts both equilibrium Super DX and DA-300, evaluated previously, were impregnated with approximately 500 ppm and 1000 ppm of both nickel and vanadium. For each catalyst this gave rise to three distinct levels of metal contamination which could be studied on the microactivity test apparatus. The equilibrium Super DX contained 190 ppm Ni and 380 ppm V or 285 ppm Ni equivalents. The impregnated Super DX catalysts had 708 and 1300 ppm nickel, 932 and 1500 ppm vanadium or 941 and 1675 ppm nickel equivalents for approximately 500 ppm and 1000 ppm Ni/V levels of impregnation (Table 10.1). Similar levels of metal impregnation were also attempted with equilibrium DA-300, which contains 694 ppm nickel, 2744 ppm vanadium or 1380 ppm nickel equivalents. The impregnated DA-300 catalysts contained 1200 and 1600 ppm nickel, and 3200 and 3800 ppm vanadium or 2000 and 2550 ppm nickel equivalents

for the same levels of impregnations as the equilibrium Super DX catalyst. Impregnation of catalysts with metals consisted of adsorption of metal salts onto the catalyst from an evaporating solution in toluene. The resulting solid was then "steamed" in a tube furnace at 1350°C with air for 8 to 12 hours. This resulted in catalysts which contained very low levels of residual carbon. Analytic data for both equilibrium and impregnated catalysts are listed in Table 10.1.

Impregnated Super DX catalysts were evaluated on the MAT with IPL VGO at 490°C and three distinct C/O ratios. MAT product yields for these tests can be found in Table 10.2. Relative to data obtained for Super DX at 475°C, results for impregnated catalysts indicate that their conversions as a function of C/O are depressed by 1.5 to 2.5 wt.% and 7.5 wt.% for 500 Ni/V and 1000 Ni/V impregnation levels, respectively (Figure 10.1). Relative to Super DX at 490°C, the depressions of conversion should be another 0.5 to 1.0 wt.% greater due to the low temperature used for the equilibrium catalyst. The slight loss of activity in the former impregnated catalyst (941 Ni equivalents) versus the latter impregnated catalyst (1675 Ni equivalents) is consistent with Davison literature, which shows Super DX loses activity rapidly at metal levels of greater than 750 Ni equivalents.

The effect of C/O on coke yield for all three Super DX catalysts and IPL VGO is shown graphically in Figure 10.2. The response of coke yield is linear, lowest for the equilibrium Super DX at 475°C and greatest for the 500 Ni/V impregnated Super DX. The coke yields can be expressed algebraically as follows:

Super DX Catalyst	Ni Equivalents	T °C	
equilibrium	285	475	coke (wt.%) = 0.9091 (C/O) - 0.773
+ 500 Ni/V	941	490	coke (wt.%) = 1.188 (C/O) + 0.030
+ 1000 Ni/V	1675	490	coke (wt.%) = 1.007 (C/O) - 0.201

Both impregnated catalysts give greater coke yields than the equilibrium catalyst at a given C/O ratio and give greater increases in coke yield with increasing C/O. This, when coupled with lower conversion at a given C/O, shows that

metals cause the catalyst to produce much more coke. This can be illustrated by considering the coke yields for these catalysts at constant conversion. For 60 wt.% conversion, IPL VGO will produce 1.98, 4.05 and 4.30 wt.% coke for equilibrium, 500 Ni/V and 1000 Ni/V impregnated catalysts, which agrees well with the order of metals contamination.

Similar MAT experiments were also carried out with Super DX impregnated catalysts and IPL 33.7% VTB/66.3% VGO. Product yields for these tests done at 490°C and three distinct C/O ratios are listed in Table 10.3. Conversion data as a function of C/O are plotted in Figure 10.3 and show that for IPL residua conversion is also depressed with increasing metals impregnation of the catalyst. Unfortunately, no MAT yield data was acquired for IPL residua with equilibrium Super DX since this catalyst was not used to study residua cracking. With Super DX impregnated at 500 ppm Ni/V and 1000 ppm Ni/V, the effect of metals on conversion for both IPL VGO and 33.7% VTB/66.3% VGO are very similar. In both cases conversion decreases from 2.5 to 7 wt.% over the C/O range of 2 to 7. In absolute terms, however, conversions are greater for the residua than for its corresponding gas oil. This was observed previously with equilibrium DA-300 catalyst.

The effect of metals impregnation on the coke/(C/O) relationship in relative terms is similar for both IPL gas oil and residua. Coke yield data, for the latter material are shown in Figure 10.4 and can be expressed as:

Super DX Catalyst	Ni Equivalents	T °C	
+ 500 Ni/V	941	490	coke (wt.%) = 2.039 (C/O) + 1.60
+ 1000 Ni/V	1675	490	coke (wt.%) = 1.763 (C/O) + 0.262

At a constant 60 wt.% conversion, Super DX impregnated with 500 ppm Ni/V gives a 6.65 wt.% coke yield while the 1000 ppm Ni/V impregnated catalyst yields only 5.80 wt.% coke. These results are the reverse of those observed for IPL VGO. This may result from 1) the impregnated catalyst not being consistent; 2) inconsistent data; or 3) the dependence of coke selectivity on feed composition.

Impregnated DA-300 catalysts were also evaluated in the MAT apparatus with IPL VGO at 490°C and three distinct C/O ratios. MAT product yields for these experiments are listed in Table 10.4. Conversion data for equilibrium DA-300 as well as 500 and 1000 ppm Ni/V impregnated DA-300 are shown graphically in Figure 10.5. For both levels of impregnation conversions are similar and are reduced 3-7 wt.% for $2 \lesssim C/O \lesssim 7$. The response of coke yield to C/O is also very similar for both levels of DA-300 impregnation (Figure 10.6). These yields, however, are much greater than those of equilibrium DA-300 at similar C/O levels:

DA-300 Catalyst	Ni Equivalents	
equilibrium	1380	coke (wt.%) = 1.121 (C/O) - 0.354
+ 500 Ni/V	2000	coke (wt.%) = 1.579 (C/O) - 0.395
+ 1000 Ni/V	2550	coke (wt.%) = 1.695 (C/O) - 0.339

At equivalent 70 wt.% conversions the equilibrium and 500 and 1000 ppm Ni/V impregnated DA-300 catalysts yield 4.05, 7.30 and 8.30 wt.% coke, respectively. This is directionally the type of increase expected, yet it is worth observing that the first 500 ppm Ni/V causes a far greater increase in coke yield than the second 500 ppm Ni/V.

DA-300 catalysts, impregnated with nickel and vanadium, were also evaluated with IPL residua (33.7 wt.% VTB/66.3 wt.% VGO) in the MAT unit. MAT product yields for these tests can be found in Table 10.5. Results show that conversion data (Figure 10.7) for IPL residua parallels that of IPL VGO as catalyst metals contamination is increased from 0 to ~1000 ppm Ni/V, i.e. conversion is reduced some 4-7 wt.% at constant C/O. As with IPL VGO, IPL residua shows only slight differences in conversion for both levels of impregnation. Nevertheless, the lower conversions are for the greatest amount of metal impregnation.

The relationships between coke and C/O are also similar for both IPL VGO and residua. Coke yields for the latter feed are plotted in Figure 10.8 and can be expressed as follows:

DA-300 Catalyst	Ni Equivalents	
equilibrium	1380	coke (wt.%) = 2.105 (C/O) - 0.642
+ 500 Ni/V	2000	coke (wt.%) = 2.017 (C/O) + 2.721
+ 1000 Ni/V	2550	coke (wt.%) = 2.281 (C/O) + 2.552

The slopes of these relationships are all similar; however, the large value for the intercepts insures that coke yield for the metals impregnated catalysts will be greater. At constant conversion (70 wt.%) these catalysts yield 5.15, 9.85 and 10.8 wt.% coke, which indicates that increased metals levels on the catalyst give rise to coke.

The net conclusion from these tests is that metals both increase coke yield and decrease conversion. To operate at constant conversion the refiner is, therefore, forced to accept even larger coke yields. This results in greater yields of gases and lower yields of liquid transportation fuels, which is not the desired result. The effects of metals impregnation appear to be similar for both Super DX and DA-300; however, the former material had low levels of metals to begin with. This suggests the latter is a superior resid cracking catalyst since it can tolerate high metals loadings.

TABLE 10.1

Metals Contents of Impregnated Equilibrium DA-300 Catalyst

Catalyst:	Super DX				DA-300			
Attempted Level of Impregnation								
Ni, ppm	0	500	1000	1000	0	500	1000	1000
V, ppm	0	500	1000	1000	0	500	1000	1000
Sb, ppm	0	0	0	500	0	0	0	500
Measured Elemental Content								
Ni, ppm	190	708	1300	1154	694	1200	1600	1584
V, ppm	380	932	1500	1400	2744	3200	3800	3899
Sb, ppm	6	6	6	482	98	98	98	600
C, %	0.14	0.07	0.21	0.07	0.15	0.07	0.12	0.07

TABLE 10.2

MAT Product Yield Data for IPL VGO and Impregnated Super DX

Test	MAT 559	MAT 558	MAT 557	MAT 565	MAT 564	MAT 563
Mass Balance, wt%	101.8	103.3	106.5	101.7	101.5	103.6
Metals Content						
Ni, ppm	708	708	708	1300	1300	1300
V, ppm	932	932	932	1500	1500	1500
T, °C	489	490	491	491	490	490
C/O, g/g	1.83	3.97	5.94	1.91	3.72	6.39
Product Yields, wt%						
H_2	0.32	0.68	0.83	0.36	0.56	0.96
CH_4	0.18	0.47	0.60	0.19	0.32	0.66
$\leq C_2$	0.84	1.93	2.42	0.94	1.49	2.64
ΣC_3	2.36	4.97	5.48	2.01	3.53	5.86
ΣC_4	4.24	9.29	10.3	3.18	6.27	10.5
ΣC_5	2.46	5.76	6.67	1.78	4.01	7.36
C_5+ gasoline	32.4	46.1	47.7	29.8	40.3	43.2
C_6+ gasoline	29.9	40.4	41.0	28.0	36.2	35.8
LCO	22.3	20.5	17.8	20.6	22.2	18.7
DO	35.7	12.3	9.23	41.5	22.8	12.6
Coke	2.21	4.78	7.10	1.97	3.41	6.39
Conversion	42.1	67.1	72.9	37.9	55.0	68.7
C_6+ gasoline/Conversion	0.710	0.602	0.562	0.739	0.658	0.521
Coke/Conversion	0.052	0.071	0.097	0.052	0.062	0.093
C_6+ gasoline/coke	13.7	8.48	5.79	14.2	10.6	5.60

FIGURE 10.1

The Effect of C/O Ratio on Conversion
for Metals Impregnated Super DX and IPL VGO

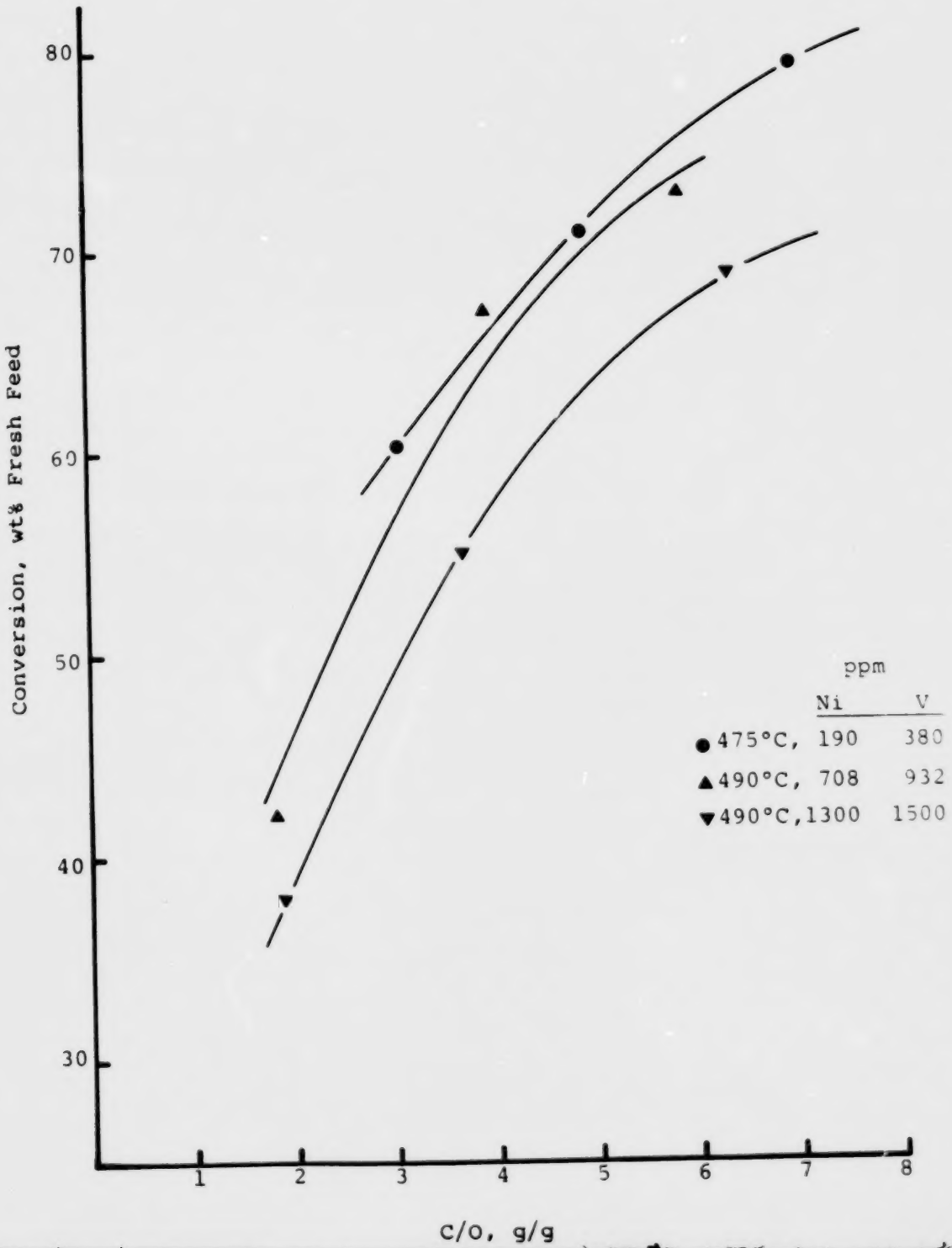


FIGURE 10.2

The Dependence of Coke Yield on C/O Ratio
for Metals Impregnated Super DX and IPL VGO

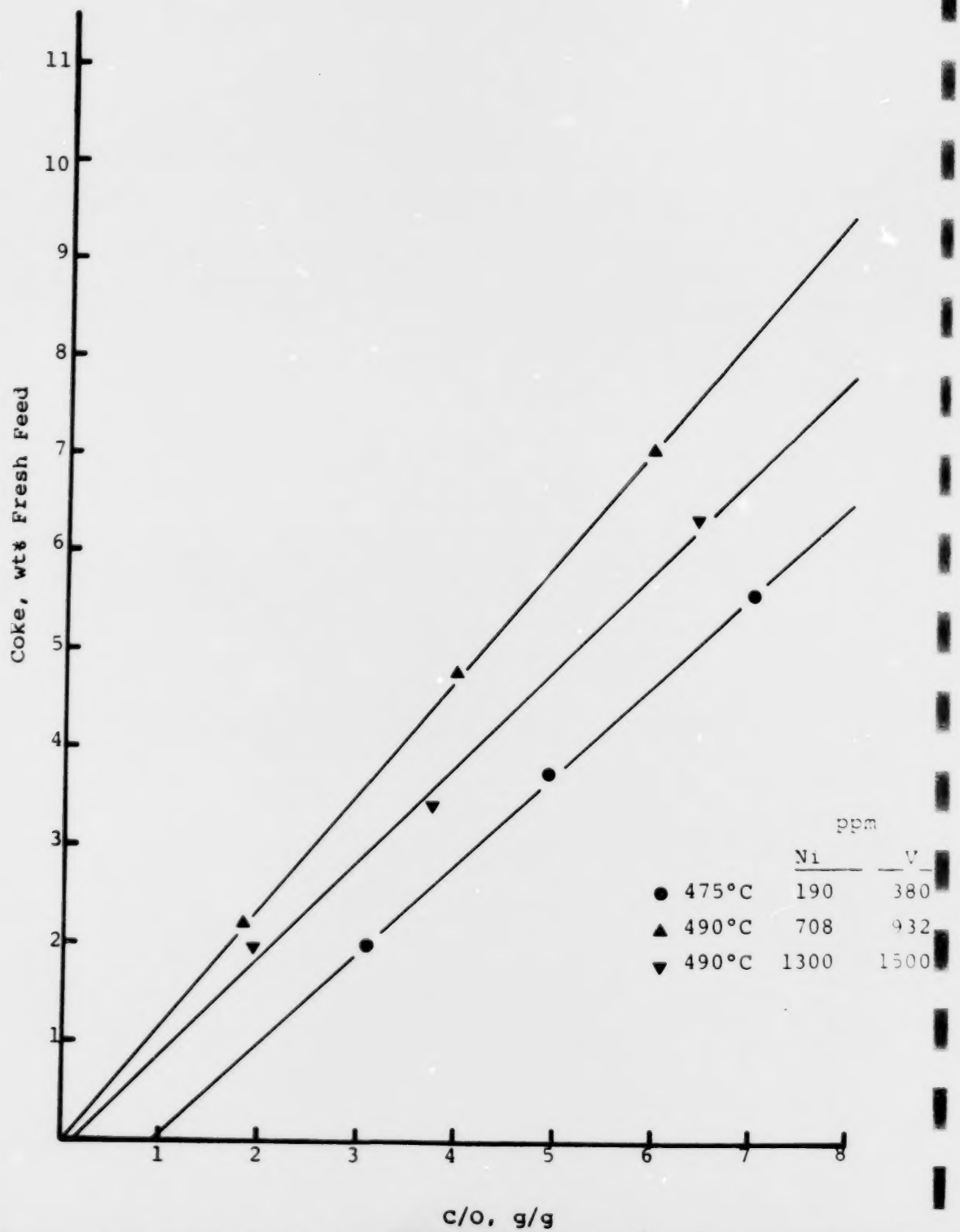


TABLE 10.3

MAT Product Yield Data for IPL 33.7% VTB/66.3% VGO and Impregnated Super DX

Test	MAT 560	MAT 562	MAT 561	MAT 566	MAT 567	MAT 568
Mass Balance, wt%	102.1	101.7	104.9	99.47	98.95	102.1
Metals Impregnation						
Ni, ppm	708	708	708	1300	1300	1300
V, ppm	932	932	932	1500	1500	1500
T, °C	491	492	490	489	491	491
C/O, g/g	2.04	4.20	5.07	2.29	4.01	6.26
Product Yields, wt%						
H_2	0.47	0.98	0.99	0.57	1.03	1.43
CH_4	0.56	0.95	0.99	0.68	0.97	1.36
$\leq C_2$	1.84	3.29	3.44	2.23	3.35	4.56
ΣC_3	3.05	5.84	5.69	3.40	5.28	7.17
ΣC_4	5.22	9.88	9.65	5.34	8.75	11.6
C_5^+ gasoline	36.6	43.3	43.7	34.0	42.9	41.8
C_6^+ gasoline	33.0	36.2	37.0	29.5	36.6	33.5
LCO	22.9	17.6	16.8	21.0	19.7	15.3
DO	24.5	10.1	8.74	29.5	13.1	7.8
Coke	5.82	9.94	12.0	4.58	6.86	11.8
Conversion	52.6	72.2	74.5	49.5	67.1	76.9
C_6^+ gasoline/Conversion	0.627	0.501	0.497	0.596	0.545	0.436
Coke/Conversion	0.111	0.138	0.161	0.093	0.102	0.153
C_6^+ gasoline/coke	5.67	3.63	3.09	6.05	5.34	2.85

FIGURE 10.3

The Effect of C/O Ratio on Conversion for Metals Impregnated Super DX and IPL 33.7% VTB/66.3% VGO

T = 490°C

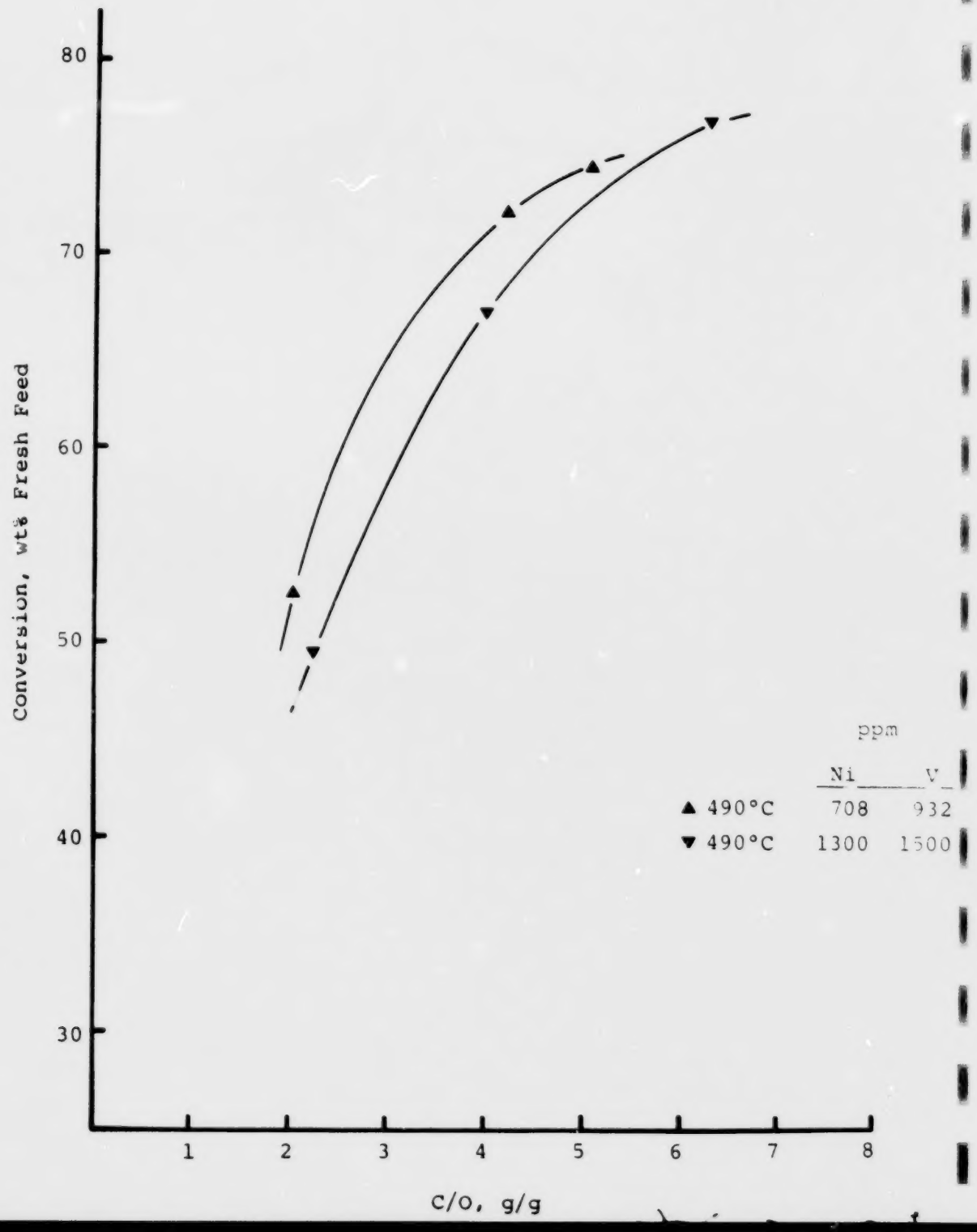


FIGURE 10.4

The Dependence of Coke Yield on C/O Ratio for Metals Impregnated Super DX and IPL 33.7% VTB/66.3% VGO

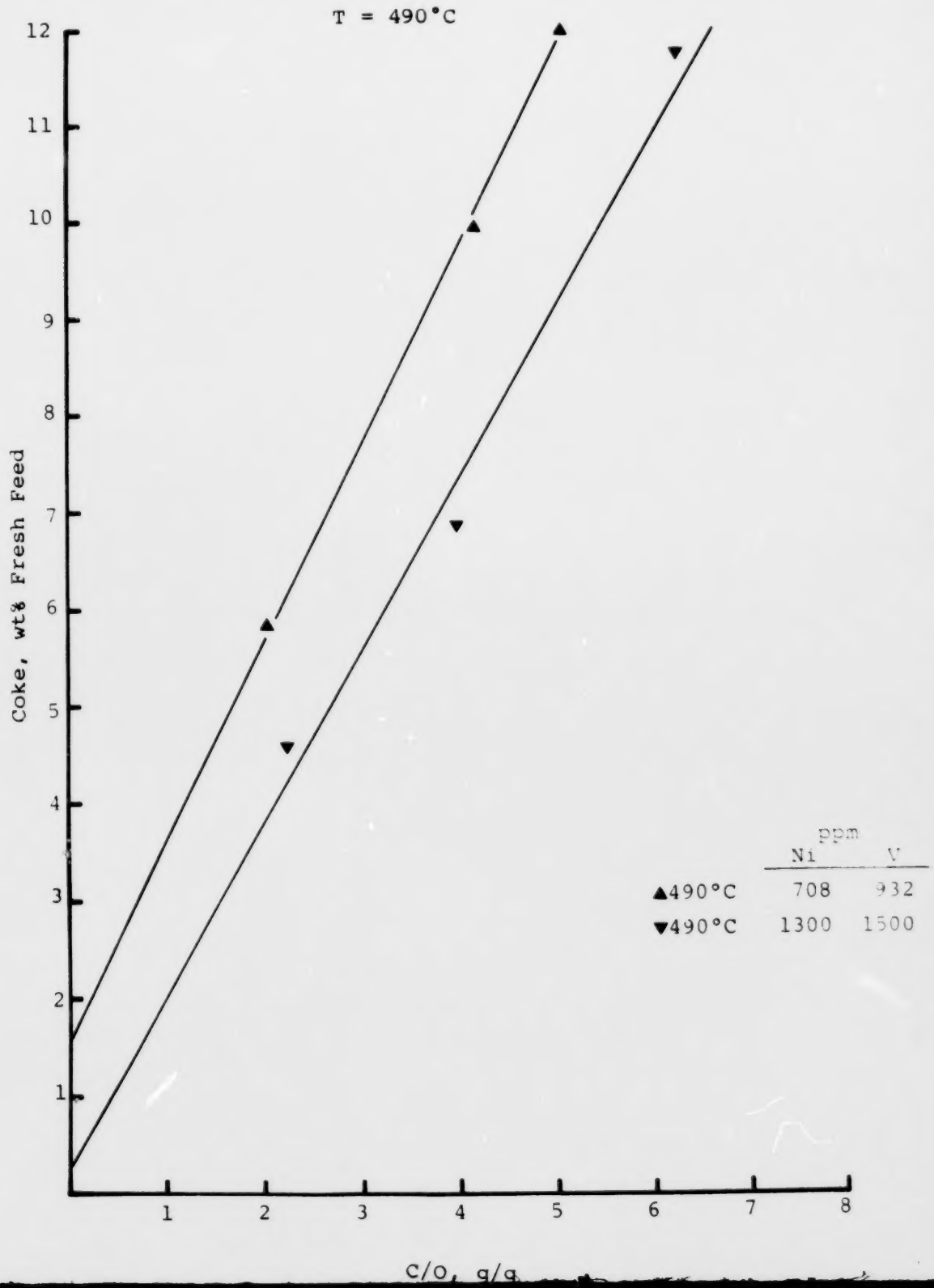


TABLE 10.4

MAT Product Yield Data for IPL VGO and Impregnated DA-300

Test	MAT 536	MAT 537	MAT 538	MAT 553	MAT 552	MAT 551
Mass Balance, wt%	101.7	105.2	106.1	101.6	105.7	105.2
Metals Impregnation						
Ni, ppm	1200	1200	1200	1600	1600	1600
V, ppm	3200	3200	3200	3800	3800	3800
T, °C	490	491	490	490	490	490
C/O, g/g	1.88	4.38	6.45	2.08	4.09	6.2
Product Yields, wt%						
H_2	0.27	0.49	0.81	0.40	0.75	1.15
CH_4	0.20	0.38	0.90	0.19	0.41	0.76
C_2	0.88	1.62	3.10	1.03	1.94	3.15
C_3	2.39	4.22	6.44	2.37	4.42	6.14
C_4	4.37	8.24	11.8	4.22	8.02	11.2
C_5	2.90	5.42	7.82	2.69	5.19	7.94
C_5^+ gasoline	31.1	48.0	45.5	32.9	43.2	43.9
C_6^+ gasoline	28.2	42.5	37.7	30.2	38.0	35.9
LCO	23.0	20.2	15.6	22.0	20.4	16.4
DO	35.6	11.6	7.47	34.2	15.1	8.94
Coke	2.71	6.14	10.0	3.26	6.86	10.3
Conversion	41.5	68.2	77.0	43.8	64.5	74.7
C_6^+ gasoline/Conversion	0.680	0.623	0.490	0.689	0.584	0.481
Coke/Conversion	0.065	0.090	0.130	0.074	0.106	0.138
C_6^+ gasoline/coke	10.5	6.92	3.77	9.31	5.56	3.48

FIGURE 10.5

The Effect of C/O Ratio on Conversion for Metals Impregnated DA-300 and IPL VGO

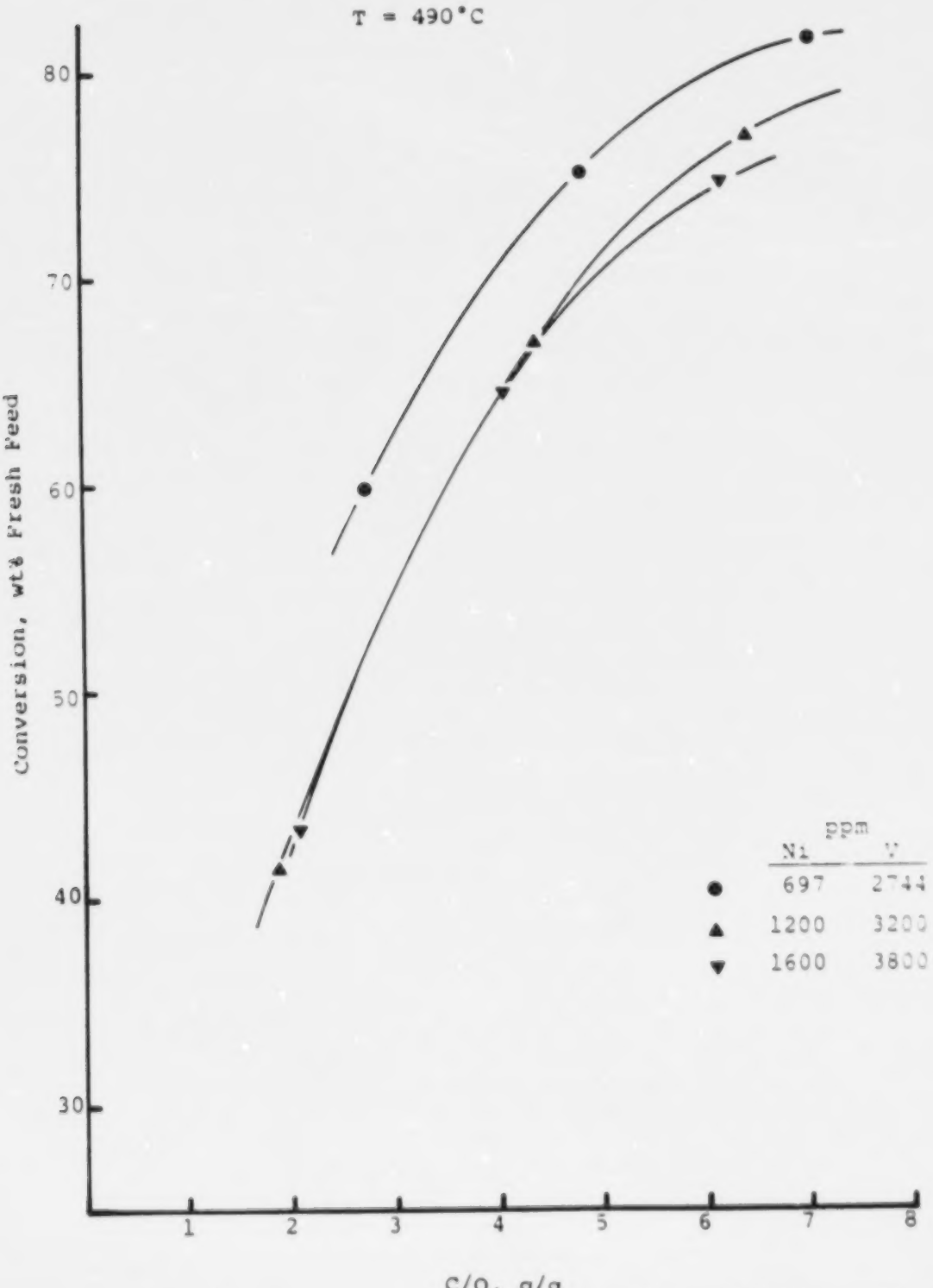


FIGURE 10.6

The Dependence of Coke Yield on C/O Ratio for Metals Impregnated DA-300 and IPL VGO

T = 490°C

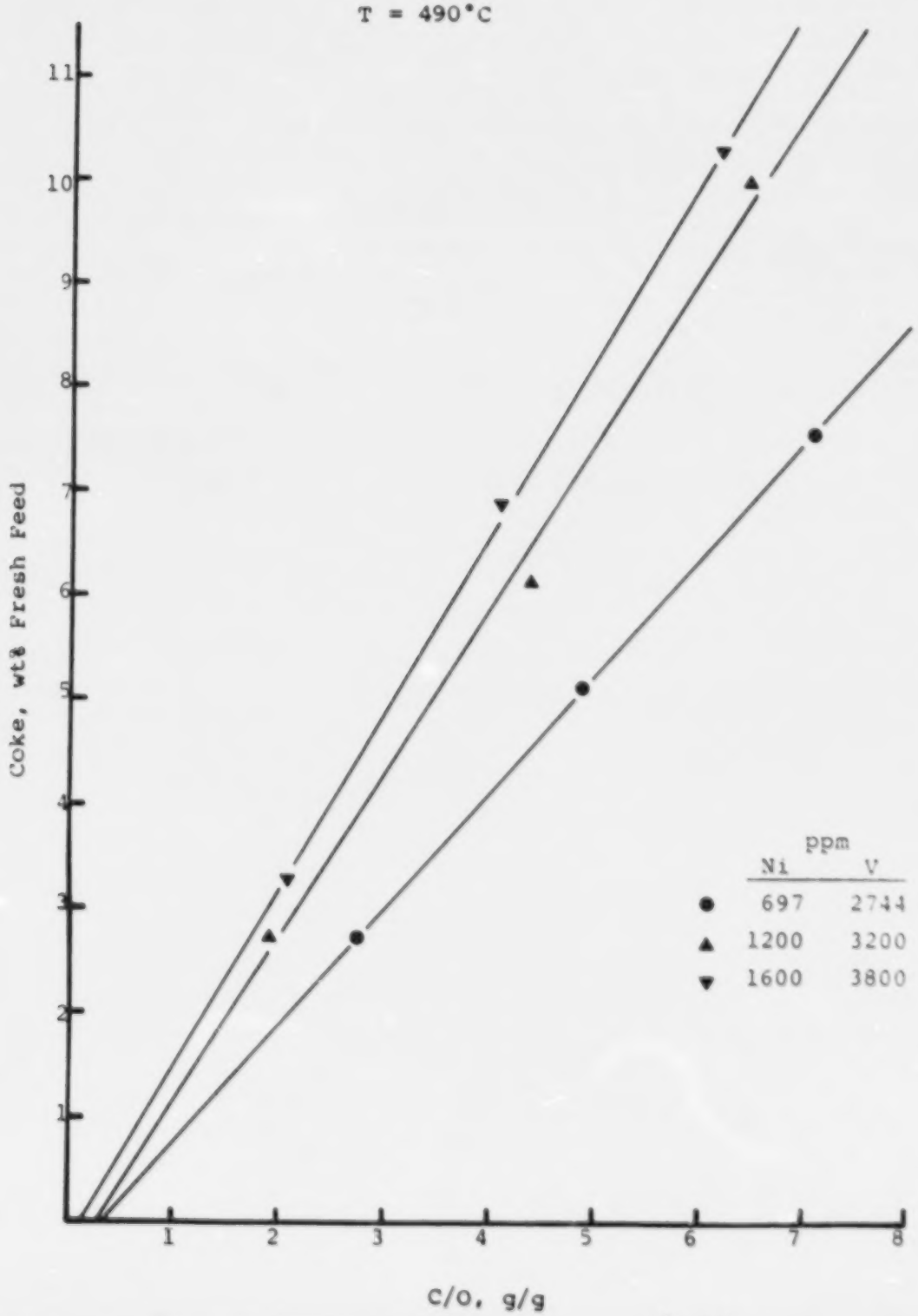


TABLE 10.5

MAT Product Yield Data for IPL 33.7% VTB/66.3% VGO and Impregnated DA-300

Test	MAT 540	MAT 539	MAT 541	MAT 556	MAT 554	MAT 555
Mass Balance, wt%	100.9	103.0	100.8	98.8	104.1	100.9
Metals Impregnation						
Ni, ppm	1200	1200	1200	1600	1600	1600
V, ppm	3200	3200	3200	3800	3800	3800
T, °C	490	490	490	490	491	490
C/O, g/g	2.06	4.06	6.17	2.05	4.19	6.08
Product Yields, wt%						
H_2	0.42	0.71	0.94	0.64	1.18	1.38
CH_4	0.62	0.84	1.27	0.65	0.99	1.15
$\leq C_2$	1.89	2.75	3.86	2.17	3.52	4.13
C_3	3.61	5.47	6.73	3.52	5.78	6.22
C_4	6.08	9.68	11.6	5.60	10.2	10.7
C_5	3.85	5.93	8.91	3.61	6.58	6.82
C_5^+ gasoline	36.0	43.8	41.0	31.3	41.8	39.5
C_6^+ gasoline	32.1	37.9	32.1	27.7	35.2	32.7
LCO	21.8	17.9	14.7	21.2	17.2	15.3
DO	23.7	9.40	6.88	28.8	9.86	7.74
Coke	6.9	10.9	15.2	7.33	11.7	16.4
Conversion	54.5	72.7	78.4	50.0	73.0	76.7
C_6^+ gasoline/Conversion	0.589	0.521	0.409	0.554	0.482	0.514
Coke/Conversion	0.127	0.150	0.194	0.147	0.160	0.213
C_6^+ gasoline/coke	4.64	3.47	2.11	3.77	3.01	2.41

FIGURE 10.7

The Effect of C/O Ratio on Conversion for Metals Impregnated DA-300 and IPL 33.7% VTB/66.3% VGO

T = 490°C

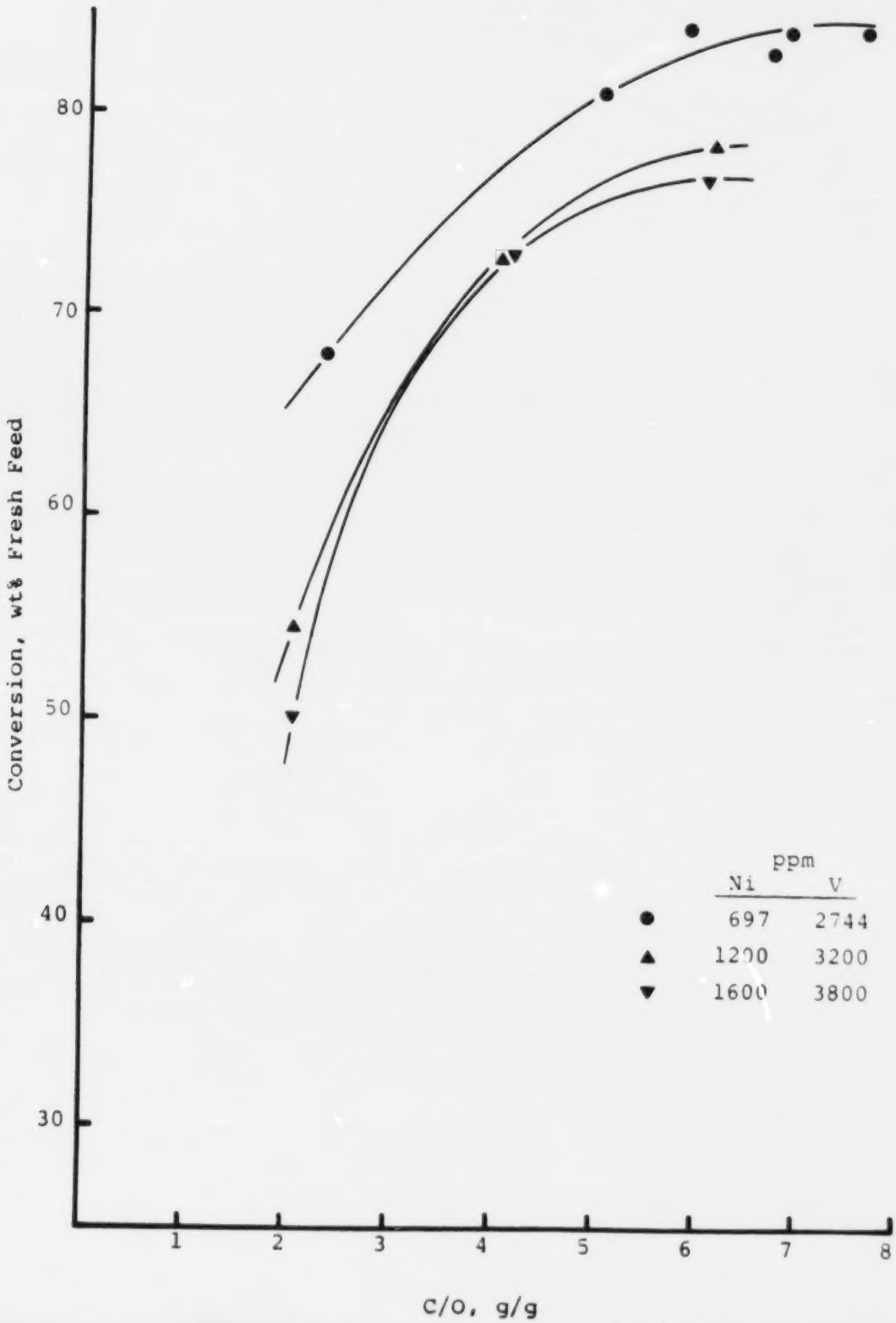
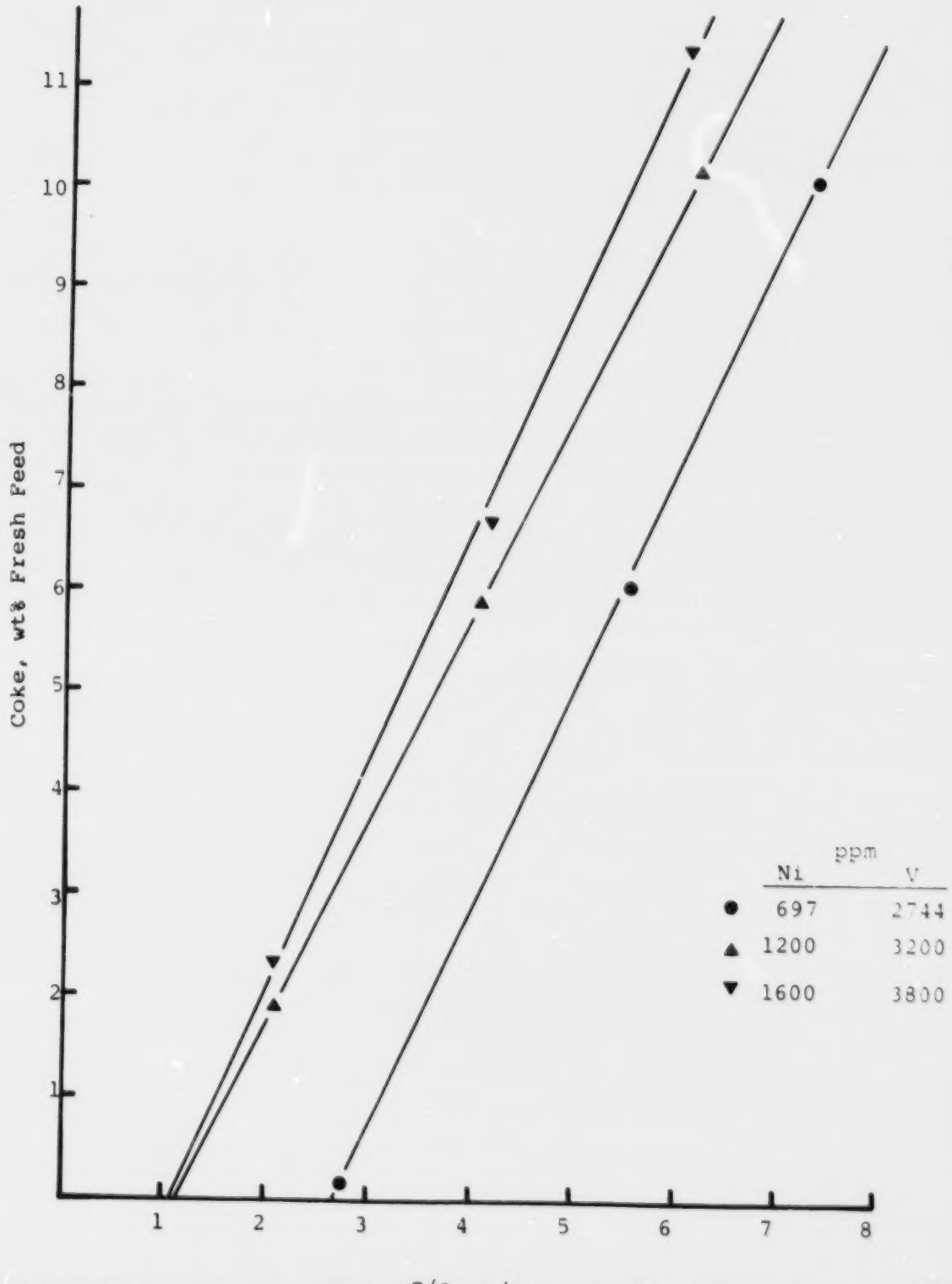


FIGURE 10.8

The Dependence of Coke Yield on C/O Ratio for Metals Impregnated DA-300 and IPL 33.7% VTB/66.3% VGO

T = 490°C



11) THE EFFECT OF ATHABASCA BITUMEN ON MAT PRODUCT YIELDS

Athabasca bitumen is currently processed into Syncrude crude oil by fluid coking and partial hydrogenation of the coked liquid products. The coker is a high temperature fluidized bed unit which thermally cracks the bitumen feed. The effect of bitumen on Syncrude gas oil cracking yields has been studied to determine the total liquid yield of bitumen from fluid catalytic cracking. Four mixtures of Athabasca bitumen in Syncrude gas oil, ranging from 13.6 to 53.3 wt.% bitumen and Syncrude gas oil, were cracked in the MAT apparatus at 490°C and C/O ~4. Product yields for each of these feeds are listed in Table 11.1 and shown graphically in Figure 11.1 as a function of bitumen content. The mixture most concentrated in bitumen (53.3 wt.%) has a Conradson carbon residue of 7.2 wt.%, which makes it similar in this respect to the most concentrated mixtures of IPL VTB/VGO and Lloydminster ATB/VGO. These Syncrude/bitumen feeds contain varying levels of sulphur, which range from 0.44 wt.% for Syncrude gas oil to 2.82 wt.% for 53.3 wt.% bitumen in Syncrude gas oil. It should be noted that the bitumen used in this study is full range material (200°C+) which is 67 wt.% residua (504°C+) Product yield data for these Athabasca bitumen/Syncrude gas oil blends parallel those obtained with IPL VTB/VGO and Lloydminster ATB/VGO mixtures. With bitumen contents of the feed increasing from 0 to 53.3 wt.%, light ends yields increase from 1.5 to 4.71 wt.%, C_3C_4 yields increase from 10.7 to 14 wt.% and coke yields increase from 3.43 to 6.77 wt.%; while C_6+ gasoline yields decrease from 39.7 to 32.5 wt.%, light cycle oil yields decrease from 23.1 to 21.9 wt.% and decant oil yields decrease from 17.8 to 14.2 wt.%. For IPL and Lloydminster blends, light ends yields also increase approximately 2 fold with residua addition. This is much less than the approximately 3 fold addition observed with bitumen mixtures. C_3C_4 yields also increase to a greater extent in relative terms for bitumen/Syncrude gas oil mixtures than IPL VTB/VGO and Lloydminster ATB/VGO mixtures. Loss in gasoline yield over the range of residua addition is greatest for bitumen/Syncrude (18.1 wt.%), less for IPL VTB/VGO (17 wt.%) and least for Lloydminster ATB/VGO (7 wt.%). Clearly, yield patterns for gasoline vary with the residuum

being cracked. Cycle oil yield patterns for all residuum/gas oil mixtures are similar and decrease slightly with increasing residua levels in the feed. The addition of residuum to gas oil results in greater yields of gases and coke and lower yields of liquid products, particularly gasoline.

Product yield data in Table 11.1 can also be used to calculate Athabasca bitumen cracking yields provided one assumes that the materials which are blended into the feed crack independently of one another. Results from these calculations are listed in Table 11.2, and, except for low levels of bitumen addition, the calculated product yields for whole bitumen are remarkably consistent. Calculated yields at low (13.3 wt.%) bitumen additions should be discounted due to the large uncertainties introduced by experimental error. Compared with Syncrude gas, Athabasca bitumen produces high yields of hydrogen (0.87 vs 0.22 wt.%), methane (1.75 vs 0.39 wt.%) and light ends (7.51 vs 1.56 wt.%) which also contains hydrogen sulphide. The yields of low molecular weight hydrocarbon (C_3s, C_4s and C_5s) are also much larger for Athabasca bitumen than for Syncrude gas oil. This is reasonable, since the latter material has been coked, resulting in the reduction of many of the constituents which form these light hydrocarbons. Athabasca bitumen yields far less gasoline than Syncrude gas oil (26.1 vs 39.7 wt.%) which makes it a very much poorer feedstock. Yields of light cycle oil are slightly lower (20.1 vs 23.1 wt.%), while yields of decant oil are markedly lower (7.95 vs 17.8 wt.%). Unfortunately, the coke yield for bitumen is very large (10.5 wt.%) relative to that of Syncrude gas oil (3.43 wt.%). If total potential liquid yields are considered (C_3s through LCO), Syncrude gas oil gives a 77.1 wt.% yield and Athabasca bitumen gives only slightly less at 73.4 wt.%. The problem with Athabasca bitumen yields is that they are largely light petroleum gases which must be upgraded by alkylation, polymerization or conversion to oxygenates. Also, the quality of these liquids, particularly with regards to sulphur content, must be evaluated.

TABLE 11.1

MAT Product Yields for Athabasca Bitumen/Syncrude Vacuum Gas Oil Mixtures and DA-300

Test	MAT 412	MAT 413	MAT 414	MAT 415	MAT 416
Mass Balance, wt%	100.8	100.8	98.2	98.0	94.0
T, °C	490	491	490	490	491
C/O, g/g	3.47	3.94	4.23	4.01	3.78
Feed Composition, wt%					
Athabasca Bitumen	0	13.3	26.6	39.8	53.3
Syncrude Vacuum Gas Oil	100	86.7	73.4	60.2	46.7
Product Yields, wt%					
H_2	0.22	0.35	0.43	0.47	0.51
CH_4	0.39	0.60	0.77	0.88	1.15
ΣC_2	1.56	2.43	3.24	3.80	4.71
ΣC_3	3.88	4.53	5.05	5.15	5.35
ΣC_4	6.84	8.01	8.56	8.93	8.92
ΣC_5	3.62	4.65	5.01	5.44	5.40
C_5+ gasoline	43.4	41.8	40.9	40.1	37.9
C_6+ gasoline	39.7	37.2	35.9	34.6	32.5
LCO	23.1	22.6	22.2	22.2	21.9
DO	17.8	15.4	14.2	13.9	14.5
Coke	3.43	5.19	5.74	5.94	6.77
Conversion	59.1	62.0	63.5	63.9	63.6
C_6+ gasoline/Conversion	0.672	0.600	0.565	0.541	0.511
Coke/Conversion	0.058	0.084	0.090	0.093	0.106
C_6+ gasoline/coke	11.6	7.17	6.28	5.82	4.82

FIGURE 11.1

The Effect of Bitumen on MAT Product Yields of Athabasca Bitumen/Syncrude VGO Mixtures with DA-300

C/O ≅4, T = 490°C

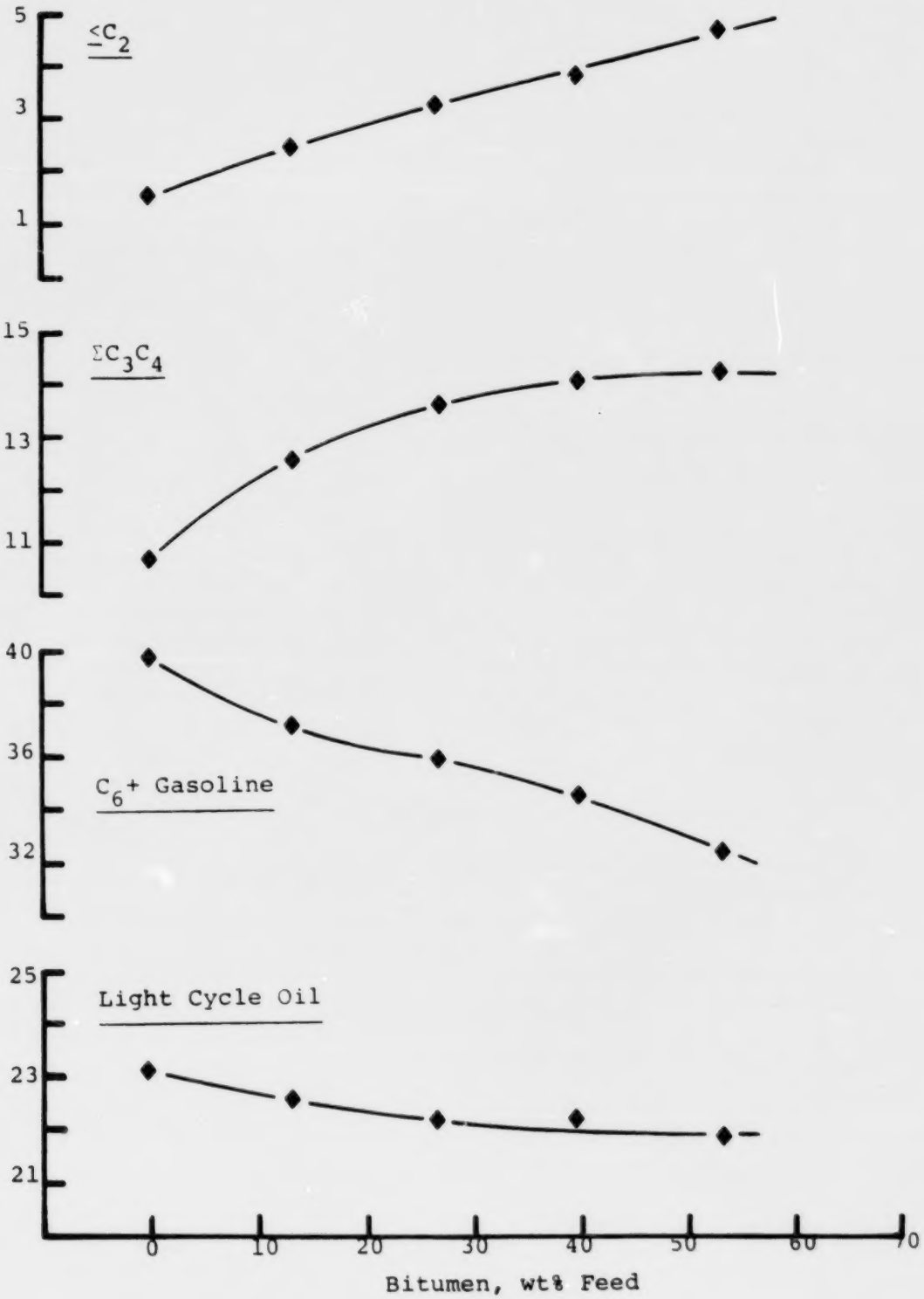


FIGURE 11.1 (Cont'd)

The Effect of Bitumen on Mat Product Yields of Athabasca Bitumen/Syncrude VGO Mixtures with DA-300

C/O ≅4, T = 490°C

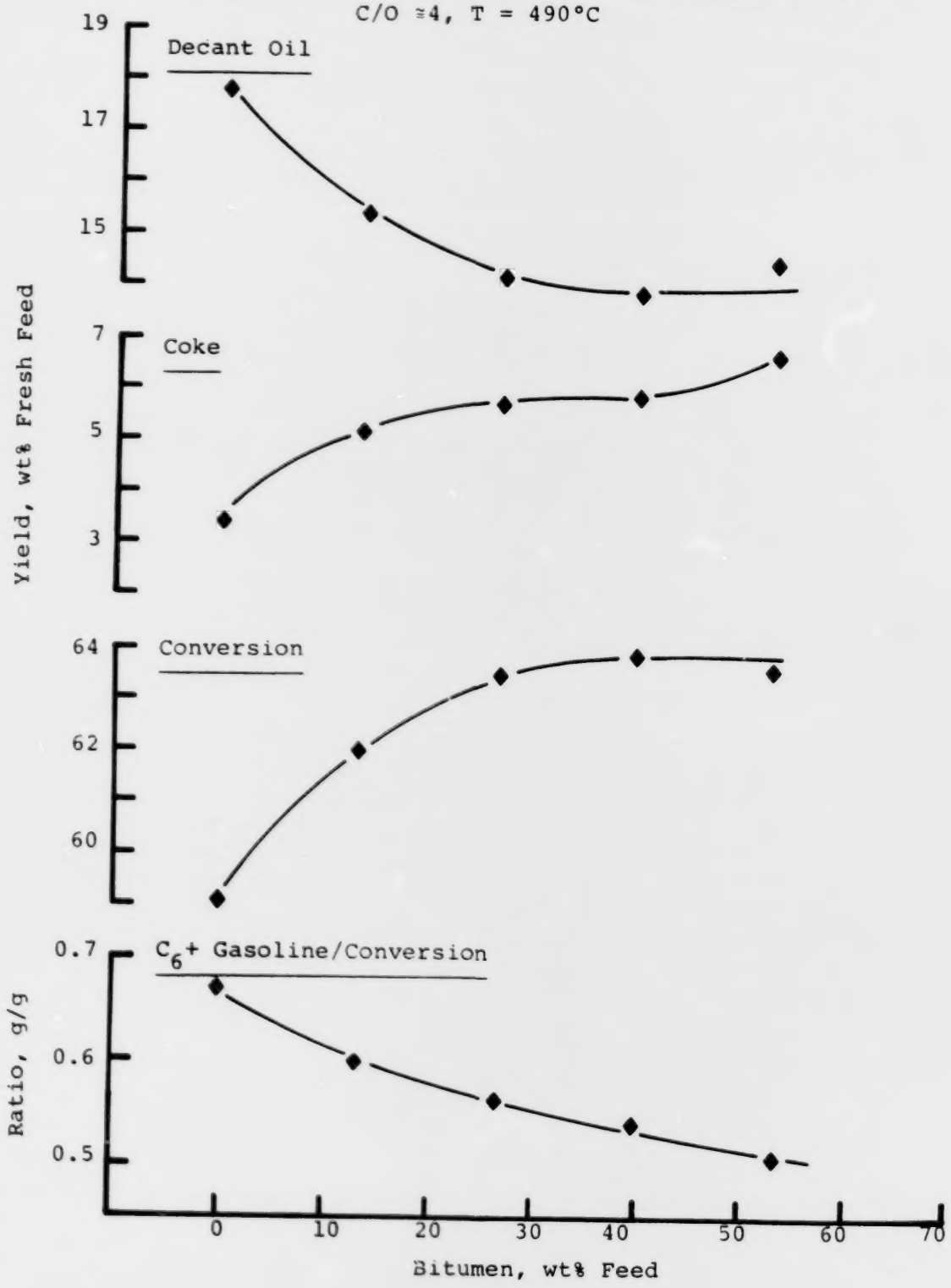


FIGURE 11.1 (Cont'd)

The Effect of Bitumen on MAT Product Yields of Athabasca Bitumen/Syncrude VGO Mixtures with DA-300

C/O ≅4, T = 490°C

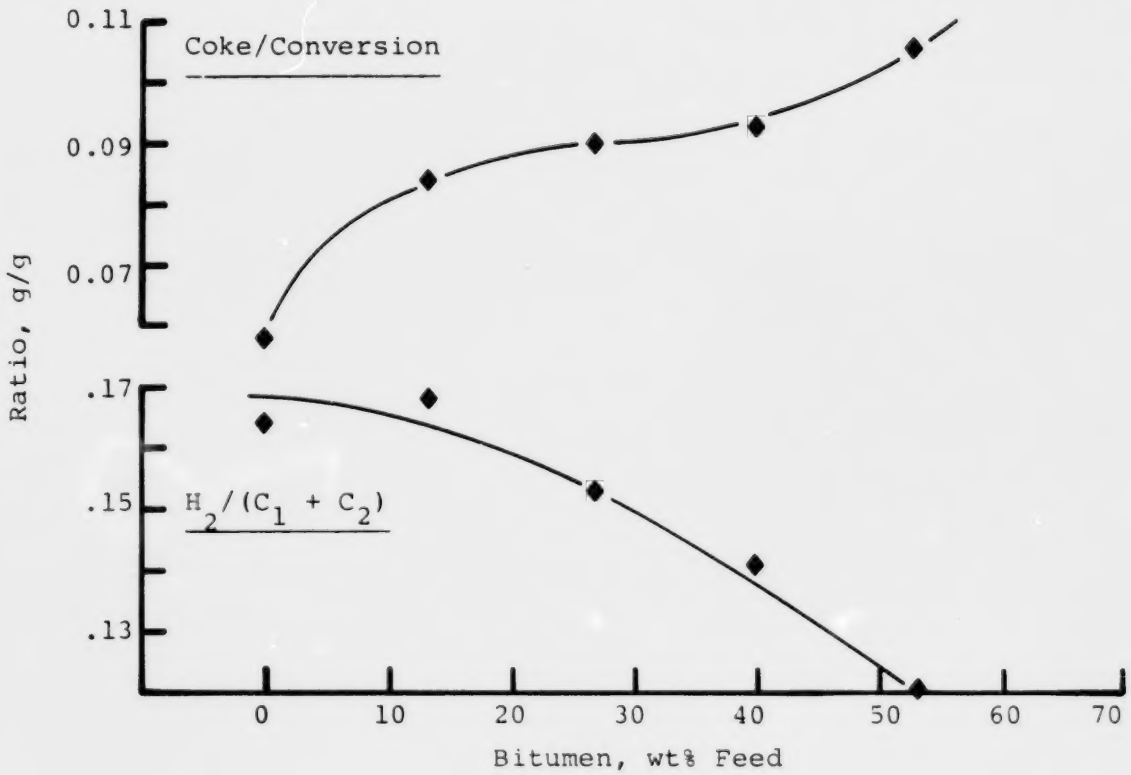


TABLE 11.2

Calculated Athabasca Bitumen Product Yields With DA-300*
(T=490°C, C/O 4)

Material	Bitumen					VGO
Test	MAT 413	MAT 414	MAT 415	MAT 416	Average**	MAT 389
Wt.% bitumen in Feed	13.3	26.6	39.8	53.3		
Product Yields, wt%						
H_2	1.20	1.01	0.85	0.76	0.87	0.22
CH_4	1.97	1.82	1.62	1.82	1.75	0.39
ΣC_2	8.10	7.88	7.19	7.47	7.51	1.56
ΣC_3	8.77	8.28	7.07	6.64	7.33	3.88
ΣC_4	15.6	13.3	12.1	10.7	12.0	6.84
ΣC_5	11.4	8.84	8.19	6.96	8.00	3.62
C_5+ gasoline	31.4	34.0	35.1	33.1	34.1	43.4
C_6+ gasoline	20.9	25.4	26.9	26.2	26.1	39.7
LCO	19.3	19.7	20.8	20.8	20.4	23.1
DO	0.2	4.26	8.00	11.6	7.95	17.8
Coke	16.7	12.1	9.74	9.70	10.5	3.43

* calculated from the weight averaged composition
** values in MAT 414, MAT 415 and MAT 416 average

12) MAT PRODUCT DATA FOR 53.3% ATHABASCA BITUMEN/ 46.7% SYNCRUDE VACUUM GAS OIL AND DA-300

A mixture of 53.3 wt.% Athabasca bitumen and 46.7% Syncrude vacuum gas oil as cracked over DA-300 catalyst at three C/O ratios for each of three temperatures. These experiments were undertaken to determine the effect of Athabasca bitumen on Syncrude vacuum gas oil MAT product yields for similar ranges of temperature and C/O ratio. The microactivity test results for these tests are listed in Table 12.1 along with the experimental conditions employed.

The effect of C/O on the conversion of the Athabasca bitumen/ Syncrude vacuum gas oil mixture is shown graphically in Figure 12.1. The results show that all conversions for the bitumen mixture are 5-10 wt.% higher than for Syncrude vacuum gas oil at similar temperatures and C/O ratios. This is similar to conversion data obtained with both IPL and Lloydminster residua. The effect of temperature on the conversion of the bitumen mixture appears to be very small, particularly for C/O greater than four. It is interesting to note that the Syncrude vacuum gas oil conversion is affected to a greater extent by temperature, even though it is a hydrotreated cracked stock. At low C/O (~3) the bitumen mixture does show an effect of temperature on conversion. Conversions for the bitumen mixture range from 50-75 wt.% and they do not appear to be levelling off at the higher end as do those of Syncrude vacuum gas oil.

Coke yields for the bitumen mixture are shown in Figure 12.3 as a function of C/O. The response of coke yield to C/O is approximately linear for the bitumen mixture over the range of temperatures (450-490°C) evaluated. Algebraically this relationship can be expressed as:

$$\text{coke yield (wt.\%)} = 1.882\ (C/O) + 0.3446$$

Similar behaviour was observed for Syncrude vacuum gas oil, where the relationship:

$$\text{coke yield (wt.\%)} = 1.167\ (C/O) - 0.75$$

was found to exist over an even wider range of temperatures (425-490°C). The bitumen mixture has both a greater slope

and intercept for its coke/(C/O) relationship than does Syncrude vacuum gas oil. This could be interpreted as due to a greater inherent tendency to form coke.

Individual product yields are shown as a function of conversion in Figure 12.3. The data shows that light end yields ($<C_2$) for the bitumen mixture are roughly three times those of Syncrude vacuum gas oil. Furthermore, the bitumen mixture light ends yields are very temperature dependent, since they are 1-1.5 wt.% greater at 490°C than at either 450 or 470°C. C_3C_4 yields are also somewhat larger than those of Syncrude vacuum gas oil; however, for both feedstocks these yields increase in a similar manner with conversion. C_6+ gasoline yield for the bitumen mixture is less than that for Syncrude vacuum gas oil over the range of conversions studied. For the former feed, a maximum C_6+ gasoline yield of 34 wt.% occurs at 65 wt.% conversion, which compares with the Syncrude vacuum gas oil C_6+ maximum of 38 wt.% at 62 wt.% conversion. Cycle oil yields, both light cycle oil and decant oil, are similar for both the bitumen mixture and Syncrude vacuum gas oil over the conversion range of 50 to 80 wt.%. The bitumen mixture does produce significantly higher coke yields than Syncrude vacuum gas oil and they rise rapidly for conversions of greater than 70 wt.%.

Product ratios (Figure 10.4) also show some interesting trends. For the bitumen mixture, the ratio of hydrogen to C_1 and C_2 hydrocarbons increases with temperature, while for Syncrude vacuum gas oil it decreases. This implies that, although bitumen is a hydrogen-deficient feedstock, disproportionately more hydrogen is rejected at higher cracking temperatures, which in turn implies greater carbon rejection (coke formation) must occur. This is reflected in the coke/conversion ratio which is particularly temperature dependent. The C_6+ gasoline/conversion ratio is also much lower for the bitumen mixture than for Syncrude vacuum gas oil.

Regression analyses (Table 12.2) for all product yields and conversion have been calculated. The coke yield, as discussed earlier, regressed to a linear equation in C/O with an excellent fit of the data ($\pm$ 0.75%) to well within experimental error. Conversion is a complicated function requiring

nearly all the parameters available in the quadratic surface. Correlations for butanes (C_4s) and C_6+ gasoline are poor and the pentanes (C_5s) correlation is particularly poor (R^2=0.3522). This is not surprising since C_5 yields can be quite variable due to the handling of reactor effluent liquid.

The mixture of 53.3 wt.% Athabasca bitumen and 46.7 wt.% Syncrude vacuum gas oil, like the other residua studied, produces more gas, LPGs and coke than its corresponding gas oil and less liquid product, particularly C_6+ gasoline.

TABLE 12.1

MAT Product Yield Data for Athabasca Bitumen in Syncrude Gas Oil (53.3/46.7) and DA-300

Test	MAT 464	MAT 467	MAT 470	MAT 465	MAT 468	MAT 471	MAT 466	MAT 469	MAT 472
Mass Balance, wt%	94.4	94.6	95.0	96.3	100.0	98.5	94.8	98.4	101.5
T, °C	450	451	450	471	470	470	491	490	490
C/O, g/g	2.80	5.70	6.33	3.00	4.78	7.60	2.72	5.85	6.25
Yields, wt% FF									
H_2	0.27	0.48	0.65	0.30	0.47	0.76	0.41	0.62	0.71
CH_4	0.53	0.65	0.82	0.64	0.82	1.19	1.09	1.32	1.57
C_2	3.06	3.98	4.53	3.17	3.98	5.36	4.55	5.39	5.90
C_3	4.63	6.62	7.43	5.07	5.85	7.55	5.76	7.47	7.26
C_4	8.40	12.1	12.0	9.44	10.2	13.1	8.42	12.5	11.7
C_5	2.82	4.12	2.83	3.66	3.37	4.25	2.27	4.31	3.66
C_5+ gasoline	30.2	36.9	34.5	34.0	37.4	35.2	35.3	35.6	35.7
C_6+ gasoline	27.4	32.7	31.7	30.3	34.0	30.9	33.0	31.3	32.1
LCO	27.7	21.0	19.0	24.2	21.7	16.2	23.9	19.5	17.9
DO	19.9	9.10	9.02	18.5	11.1	8.01	16.8	9.23	9.31
Coke	6.13	10.3	13.5	5.69	9.86	14.6	5.27	10.3	12.2
Conversion	52.4	69.9	71.9	57.4	67.2	75.7	59.3	71.3	72.8
C_6+ gasoline/Conversion	0.523	0.468	0.441	0.528	0.506	0.408	0.556	0.439	0.441
Coke/Conversion	0.117	0.147	0.188	0.099	0.147	0.193	0.089	0.144	0.168
C_6+ gasoline/coke	4.47	3.18	2.35	5.33	3.44	2.11	6.25	3.05	2.63

FIGURE 12.1

The Effect of C/O Ratio on Conversion for 53.3% Bitumen/46.7% Syncrude VGO and DA-300

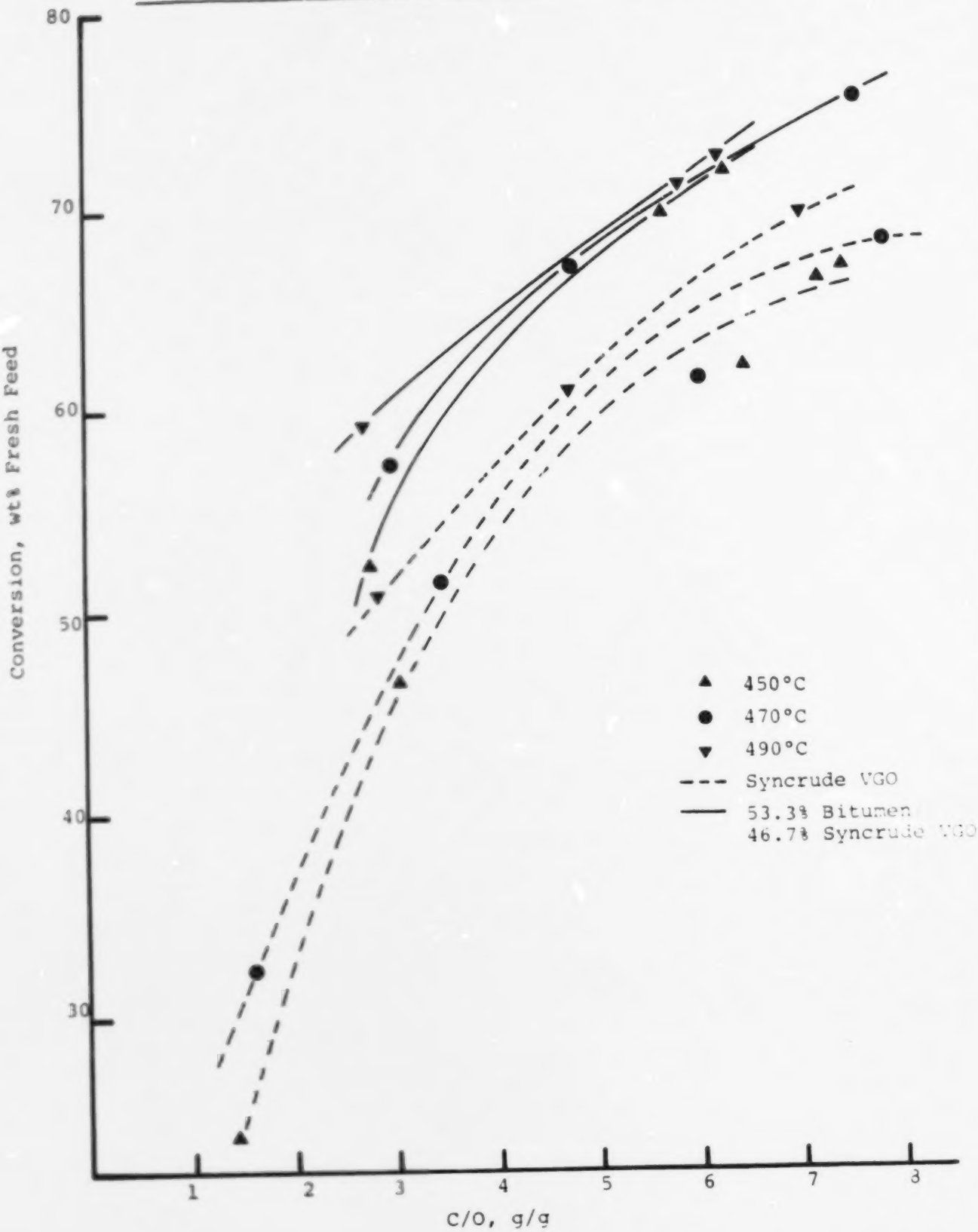


FIGURE 12.2

The Dependence of Coke Yield on C/O Ratio
for 53.3% Bitumen/46.7% Syncrude VGO and DA-300

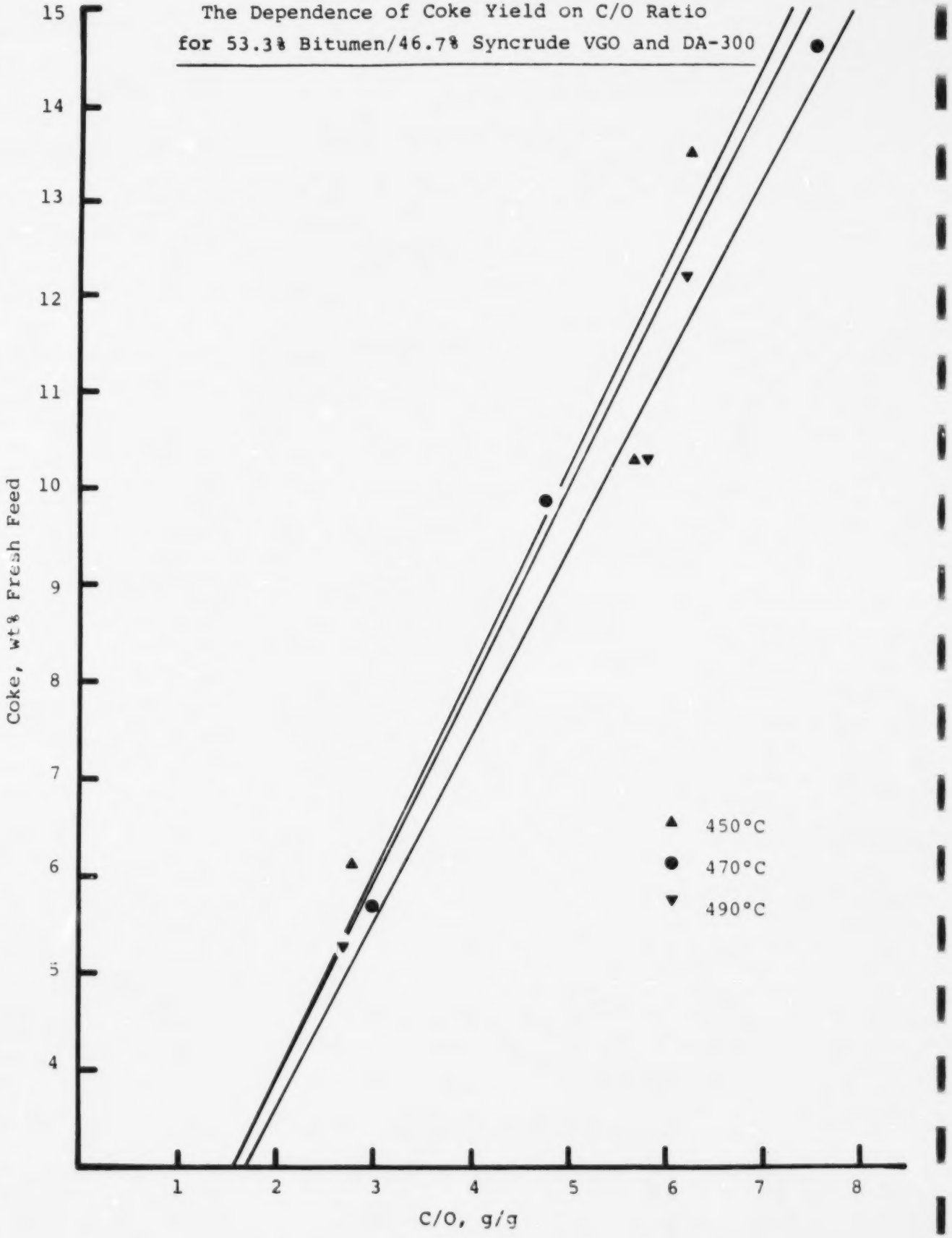
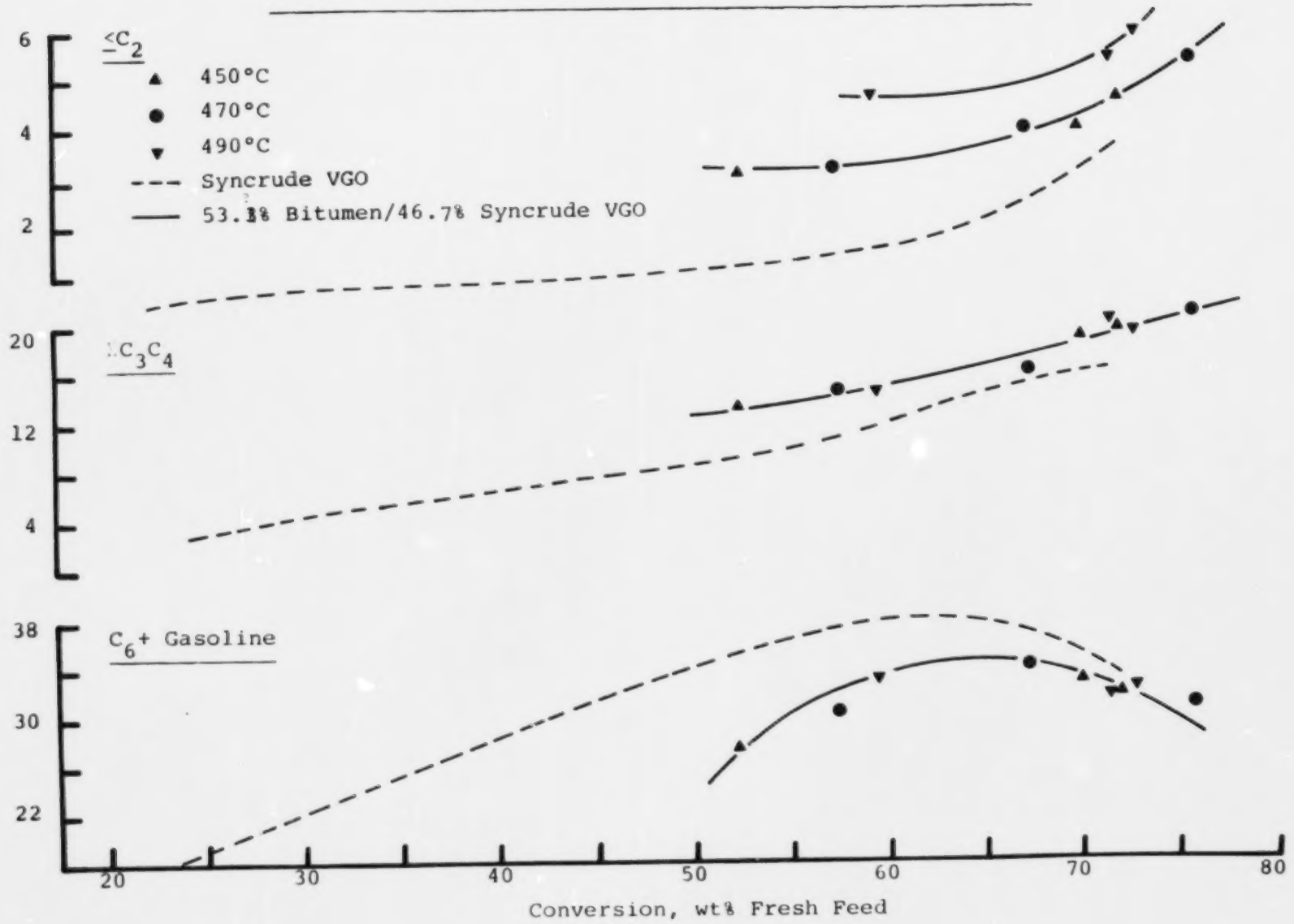


FIGURE 12.3

The Effect of Conversion on MAT Product Yields of 53.3% Bitumen/46.7% Syncrude VGO and DA-300



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The Effect of Conversion on MAT Product Yields of 53.3% Bitumen/46.7% Syncrude VGO and DA-300

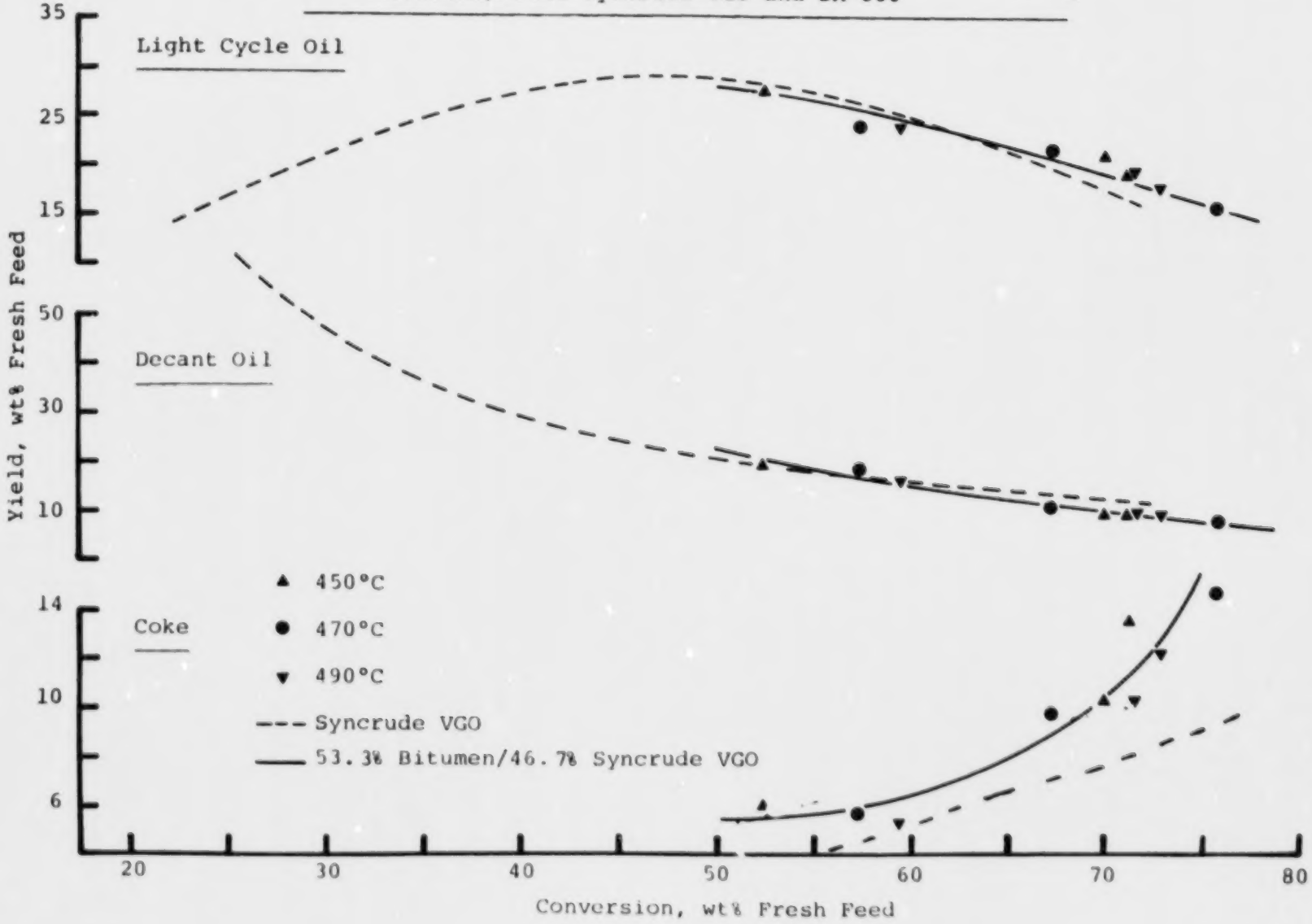


FIGURE 12.4

The Effect of Conversion on MAT Product Ratios of 53.3% Bitumen/46.7% Syncrude VGO and DA-300

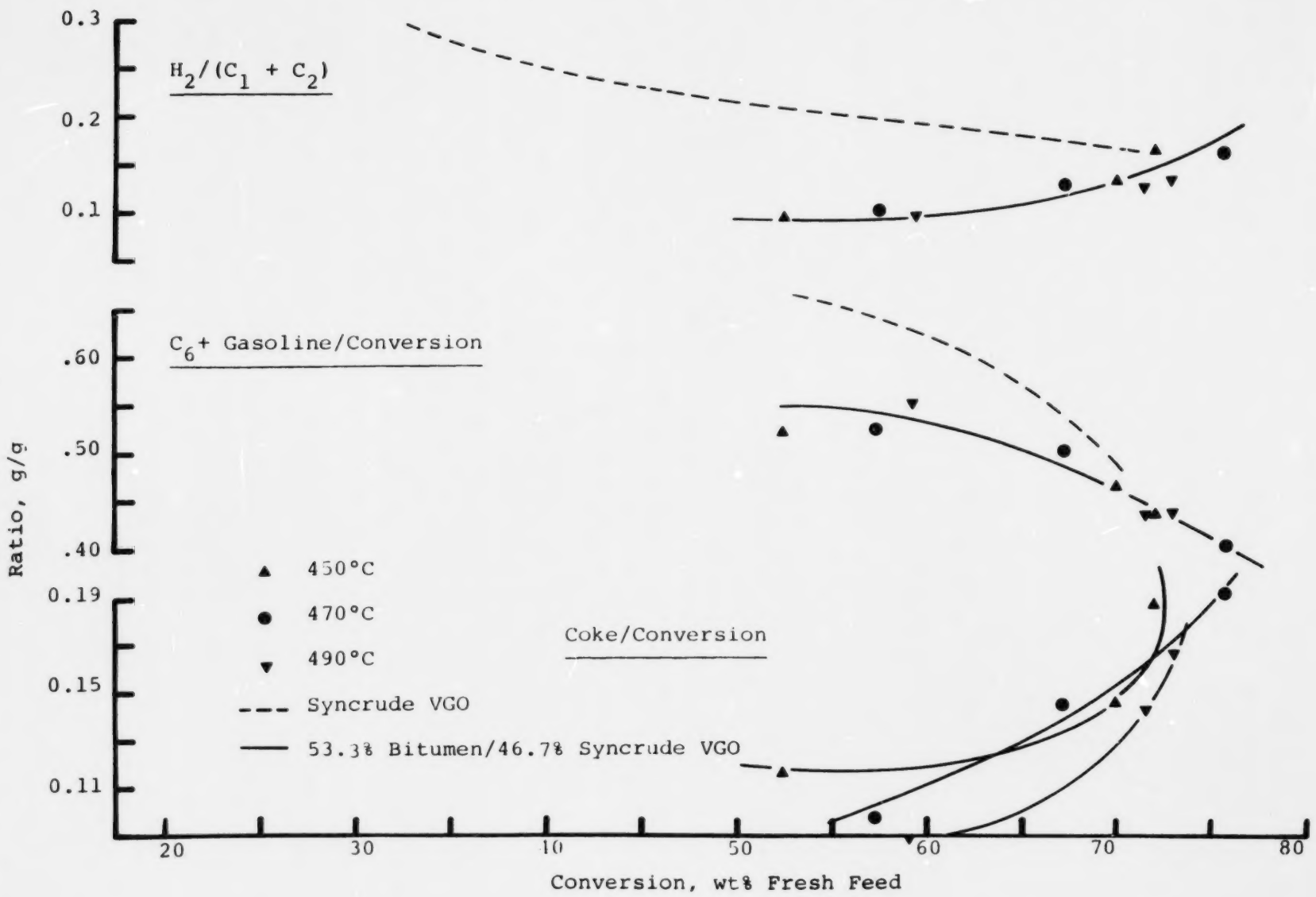


TABLE 12.2

Summary of Regression Analyses for 53.3% Bitumen/46.7% Syncrude VGO and DA-300

Component Yield (wt.%) = $a + b(T) + c(CON) + d(T)(CON) + e(T^2) + F(CON^2)$

Component	a	b	c	d	e	f	R^2	Root MSE %
H_2	2.7343		-0.1070		2.0862E-05	0.0009907	0.9666	0.0407
ΣC_2	253.8313	-1.0290	-0.5835		0.001128	0.005252	0.9886	0.1496
ΣC_3	247.9828	-1.0538			0.001126	0.001032	0.9641	0.2668
ΣC_4	3.5546					0.001637	0.8944	0.6226
ΣC_5	1.6448					0.0004097	0.3522	0.6153
C_6^+ gaso.	-107.8517		4.2879			-0.03254	0.8580	0.8283
LCO	113.3954	-0.2866		0.003820		-0.01717	0.9852	0.5509
DO	-68.9761	0.3859		-0.005322		0.01480	0.9886	0.6328

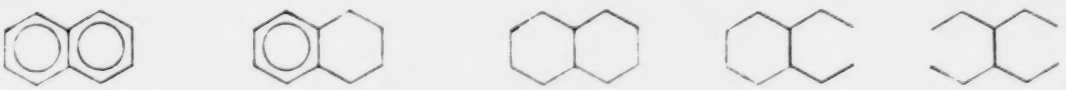
Coke Yield (wt.%) = 0.3446 + 1.882 (C/O) — R^2 = 0.9582, Root MSE % = 0.75

Conversion (wt.%) = -109.81 + 30.92 (C/O) + 0.3065 (T) - 0.0463 (C/O)(T) - 0.4882 $(C/O)^2$ — R^2 = 0.9988, Root MSE % = 0.39

where T = reactor temperature, °C
C/O = catalyst to oil ratio, g/g
CON = conversion, wt.%

13) AN EFFECT OF COMPOSITION ON CRACKING YIELDS

Syncrude vacuum gas oil is a low activity feedstock which produces relatively low yields of gasoline and high yields of cycle oils. This has been attributed to its unique composition, which is due to its processing and includes coking as well as partial hydrogenation to impart stability. Syncrude vacuum gas oil contains low levels of paraffins and monocycloparaffins and high levels of condensed cycloparaffins, monoaromatics and polynuclear aromatics. Further hydrogenation of these materials can give progressive hydrocarbon class conversions such as:



diaromatic — benzocyclo paraffin — condensed cyclo paraffin — mono cyclo paraffin — paraffin

The first two reactions involve only hydrogen addition and occur at mild hydrotreating conditions, while the latter two reactions involve the rupture of a carbon-carbon bond and, therefore, must occur under more severe conditions. The effect of converting Syncrude vacuum gas oil components to more saturated classes should improve the quality of the treated product as a cracking feedstock. However, the question arises as to the degree of hydrotreating/hydrocracking required to achieve optimum liquid and gasoline yields.

In order to do this evaluation, without actually doing any hydrogenation, it was observed that Syncrude vacuum gas oil and lubricant plant byproduct gas oil boiling range streams reflect the above series of compositional changes. Physical properties for Syncrude vacuum gas oil, Waxy 80N, Foots Oil and slack wax are found in Table 13.1. All these materials are gas oil boiling range materials with similar viscosities, no detectable nickel or vanadium content and very low levels of Conradson carbon residue. The Syncrude vacuum gas oil contains a reasonable sulphur level (0.438 wt.%) while all

lubricant plant streams contain very low levels of both impurities due to their feedstock source and hydrotreating they have experienced. The API gravity of Syncrude vacuum gas oil is low, 17.3°, while for Waxy 80N, Foots Oil and Slack Wax it is progressively much greater, 34.1, 34.6 and 38.5°, respectively. Similar trends occur with aniline points. Syncrude vacuum gas oil has an aniline point of 61.1°C while Waxy 80N, Foots Oil and Slack Wax have aniline points of 100.2, 109.1 and 119.2°C, respectively. The gravity and aniline point data suggest greater paraffin content for the series Syncrude vacuum gas oil, Waxy 80N, Foots Oil and Slack Wax which is confirmed by compositional data.

For the series of materials, compositional data are tabulated in Table 13.2. Syncrude vacuum gas oil contains 6.47 wt.% paraffins and 9.76 wt.% cycloparaffins, which is very different from the increasing paraffin content (33.1, 45.7 and 76.6 wt.%) and decreasing monocycloparaffin content (30.1, 25.0 and 9.0 wt.%) of Waxy 80N, Foots Oil and Slack Wax, respectively. Monoaromatics levels are large for Syncrude vacuum gas oil (7.11 wt.% alkylbenzenes, 5.89 wt.% benzocycloparaffins and 5.50 wt.% benzodicycloparaffins), approximately half as large for Foots Oil and very small for both Waxy 80N and Slack Wax. Similarly, Syncrude vacuum gas oil contains 35.3 wt.% polynuclear aromatic species, polar and aromatic sulphur compounds; while Foots oil, Waxy 80N and Slack Wax have 3.49, 2.20 and 0.8 wt.% levels of these refractory components. In terms of gas and gasoline precursors, this implies Syncrude vacuum gas oil contains 64.8 wt.% while Waxy 80N, Foots Oil and Slack Wax contain 97.8, 96.5 and 99.2 wt.%, respectively. All hydrotreated feeds have an extremely large potential to form gas and gasoline since paraffins, all cycloparaffins and all monoaromatics are considered "crackable"; this can be substantiated by microactivity testing.

Microactivity tests were carried out with the above series of materials using equilibrium Super DX catalyst, which has a high gasoline selectivity. The feedstocks were cracked at variable conditions of temperature and C/O ratio so that product yields over a wide range of conversions could be

obtained. MAT product yields for Syncrude vacuum gas oil, Waxy 80N, Foots Oil and Slack Wax with equilibrium Super DX are listed in Tables 13.3, 13.4, 13.5 and 13.6, respectively. For each set of data, product yields as a function of conversion are shown graphically in Figure 13.1. Note that much higher conversions is obtainable with the hydrotreated materials since they contain much more gas and gasoline precursors than the Syncrude vacuum gas (96-99 versus 64.8%).

Light ends yields for all hydrotreated materials were very low (<1 wt.%) even up to 85 wt.% conversion. Syncrude vacuum gas oil yields ~1 wt.% light ends up to 65 wt.% conversion and their yield increased rapidly with higher conversion (5.27 wt.% at 72.5 wt.% conversion) simply because conversion precursors are used up and secondary cracking predominates. C_3C_4 yields increase similarly with conversion for all feedstocks; however, over the overlapping 55-70 wt.% conversion range studied the Syncrude material yields approximately 3 wt.% more C_3C_4s.

C_6+ gasoline yield is far superior and similar for all hydrotreated materials studied. Waxy 80N, Foots Oil and Slack Wax yield 50-55 wt.% gasoline at 76 wt.% conversion, while Syncrude vacuum gas oil gave only 40 wt.% gasoline at 65 wt.% conversion. Clearly, the fully saturated materials produce much more gasoline over the entire conversion range than the Syncrude feed. This is due again to the higher precursor level. Note these materials do not contain large concentrations of partially hydrogenated polyaromatics, such as benzocycloparaffins or benzodicycloparaffins. The effect of such species on yields should be determined so that the cracking yields of the complete range of hydrogenated species are known. As far as gasoline yield is concerned, complete saturation of the feedstock to cycloparaffins is sufficient to assure maximum gasoline yields.

Light cycle oil yields for Syncrude vacuum gas oil and all hydrogenated feeds are similar for conversions of 65 wt.% and greater. The Syncrude feed gives a shallow light cycle oil yield maximum of 25 wt.% at 50 wt.% conversion, while the other materials produce a maximum 22 wt.% light cycle oil at

55 wt.% conversion. Differences can again be attributed to precursor levels, which for light cycle oil are greater for the Syncrude feed. Yields also have nothing to do with quality and while present data are not sufficient to evaluate quality, it should be anticipated that the hydrogenated feeds will produce superior light cycle oils. This should be confirmed experimentally.

Decant oil yields for Syncrude and hydrogenated feeds all decrease with increased conversion, as is typical for all cracking feedstocks. The decant oil yields for the Syncrude materials are ~2% lower over all similar conversions; however, quality of the decant oil is unknown. For the hydrotreated materials coke yields are extremely low (≤1 wt.%) up to 75 wt.% conversion, whereupon they increase rapidly with conversion. The Syncrude vacuum gas oil produces much more coke (3 wt.%) up to 65 wt.% conversion and then has its coke yield increase to >7 wt.% for conversions of only 72.4 wt.%. Differences in coke yields are due to precursor levels such as three ring polynuclear aromatics and larger polynuclear aromatics in Syncrude vacuum gas oil.

From the above product yields it can be inferred that hydrogenation of polynuclear aromatic species in cracking feedstocks such as Syncrude vacuum gas oil will increase the potential gasoline yield and conversion of such materials. The hydrogenated product need only be saturated, for the cycloparaffinic Waxy 80N and paraffinic Slack Wax give similar MAT product yields. The above data do not suggest what occurs with partially hydrogenated species such as benzocycloparaffins. In our calculation of gas and gas precursors we have assumed they will crack. Work published on the thermal cracking of such species suggests they will not crack but condensed cycloparaffins will [10, 11]. This perhaps should be investigated further since it will suggest the minimum degree of hydrogenation required to obtain an optimum cracking feedstock.

TABLE 13.1

Physical Properties of "Special" MAT Feeds

Feed		Syncrude Vacuum Gas Oil	Waxy 80N	Foot's Oil	Slack Wax
°API (ASTM D4052-81)		17.3	34.1	34.6	38.5
Specific Gravity @ 15°C		0.9509	0.8540	0.8518	0.8324
Aniline Pt., °C (ASTM D611)		61.1	100.2	109.1	119.2
Viscosity, cSt @ 100°C (ASTM D445)		8.068	3.21	7.11	4.78
Conradson Carbon Residue, wt% (ASTM D4379)		0.07	0.01	0.04	<0.01
S, wt% (ASTM D2622)		0.438	0.00035*	0.25	<0.01
N, wt% (ASTM D3431)		0.132	<0.0003	0.0019	0.00034
Metals, ppm (GCM 239)					
Ni		<0.05	<0.05	<0.05	<0.01
V		<0.05	<0.05	<0.05	<0.05
Distillation Data (GCM 379)	IBP, °C	344	293	351	284
	5%	364	328	390	346
	10%	372	339	414	369
	30%	395	364	461	412
	50%	419	380	489	452
	70%	446	398	513	496
	90%	491	420	545	549
	95%	511	432	561	570
	FBP	577	478	636	615

* ASTM D4294

TABLE 13.2

Compositions of "Special" MAT Feeds

Feed	mass %			
	Syncrude Vacuum Gas Oil	Waxy 80N	Foot's Oil	Slack Wax
Hydrocarbon Type				
Paraffins	6.47	33.1	45.7	76.6
Monocycloparaffins	9.76	30.1	25.0	9.0
Condensed Cycloparaffins	30.0	32.0	15.5	11.1
Alkylbenzenes	7.11	0.5	4.74	1.1
Benzocycloparaffins	5.89	1.2	2.80	0.8
Benzodicycloparaffins	5.50	0.9	1.87	0.6
Diaromatics	15.4	1.5	2.22	0.8
Triaromatics	8.19	0.2	0.37	0
Tetraaromatics	3.36	0.5	0.0	0
Polyaromatics & Polars	5.83	0	0.1	0
Aromatic Sulphur				
2-Ring Compounds	0.64	0	0.75	0
3-Ring Compounds	1.79	0	0.05	0
4-Ring Compounds	0.04	0	0	0
Total	100	100	100	100

TABLE 13.3

MAT Product Yield Data for Syncrude Vacuum Gas Oil and Davison Super DX

Test	201-RD	200	199	202-RD	203	204
Mass Balance, wt%	96.8	102.7	100.1	100.5	90.3	103.1
T, °C	501	477	452	455	428	428
C/O, g/g	7.90	6.73	7.00	2.92	3.33	1.77
Yields, wt% FF						
H_2	0.14	0.07	0.06	0.02	0.06	0.02
CH_4	1.80	0.48	0.52	0.23	0.19	0.03
ΣC_2	5.27	1.69	1.91	0.85	1.23	0.22
ΣC_3	6.96	4.66	4.82	2.32	2.81	0.35
ΣC_4	8.07	8.07	8.61	4.27	3.93	0.49
ΣC_5	8.04	6.97	7.24	3.44	4.77	1.09
C_5+ gasoline	46.0	47.3	45.8	38.3	36.1	19.5
C_6+ gasoline	38.0	40.3	38.6	34.9	31.3	18.4
LCO (220-344°C)	17.8	22.6	22.3	25.8	22.8	19.8
DO (344°C+)	9.78	12.2	12.8	27.0	30.9	58.2
Coke	6.05	3.52	3.73	1.47	2.28	1.43
Conversion	72.4	65.2	64.9	47.2	46.3	22.0
C_6+ gasoline/Conversion	0.525	0.618	0.595	0.739	0.676	0.836
Coke/Conversion	0.0836	0.0540	0.0575	0.0311	0.0492	0.0650
C_6+ gasoline/coke	6.28	11.4	10.3	23.8	13.7	12.9

TABLE 13.4

MAT Product Yield Data for Waxy 80 Neutral and Davison Super DX

Test	MAT 135	MAT 136	MAT 131	MAT 132	MAT 153	MAT 152	MAT 173	MAT 161
Mass Balance, wt%	101.9	101.5	100.9	104.0	98.9	93.7	100.5	99.4
T, °C	450.2	450.2	453.31	451.7	425.9	427.4	423.4	424.8
C/O, g/g	7.11	8.05	3.86	3.82	3.26	3.16	2.02	0.92
Yields, wt% FF								
H_2	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.18	0.19	0.10	0.07	0.07	0.06	0.03	0.03
H_2S	0.05	0.00	0.00	0.00	0.03	0.00	0.04	0.02
ΣC_2	0.99	0.99	0.58	0.45	0.34	0.29	0.27	0.12
ΣC_3	5.50	5.78	4.85	3.84	3.00	2.30	1.71	1.16
ΣC_4	13.5	14.1	11.4	8.92	7.62	6.57	4.08	3.06
ΣC_5	8.32	8.73	6.17	5.66	4.97	4.78	3.30	2.11
C_5^+ gasoline	61.5	59.7	60.2	60.4	50.6	51.3	44.3	32.9
C_6^+ gasoline	53.2	51.0	53.9	54.7	45.7	46.5	41.0	30.8
LCO (220-344°C)	12.3	13.0	15.7	17.8	22.3	22.7	21.8	20.4
DO (344+°C)	4.02	4.05	6.38	7.47	15.4	16.1	27.3	42.2
Coke	2.21	2.42	1.08	1.11	0.72	0.79	0.57	0.19
Conversion, wt% FF	83.7	83.0	77.9	74.7	62.3	61.2	50.9	37.4
C_6^+ gasoline/Conversion	0.639	0.614	0.692	0.732	0.733	0.760	0.806	0.824
Coke/Conversion	0.0264	0.0292	0.0139	0.0149	0.0116	0.0129	0.0112	0.0051
C_6^+ gasoline/coke	24.2	21.1	49.8	49.1	63.2	58.9	72.0	16.1

TABLE 13.5

MAT Product Yield Data for Foot's Oil and Davison Super DX

Test	MAT 137	MAT 138	MAT 144	MAT 143	MAT 157	MAT 174	MAT 163
Mass Balance, wt%	103.5	102.1	91.9	101.6	100.2	99.1	96.6
T, °C	449.0	449.0	452.01	454.4	432.1	422.7	420.7
C/O, g/g	7.19	6.86	4.08	3.61	3.43	1.94	0.98
Yields, wt% FF							
H_2	0.02	0.02	0.01	0.01	0.01	0.01	0.01
CH_4	0.33	0.29	0.11	0.13	0.09	0.03	0.05
H_2S	0.00	0.07	0.08	0.07	0.19	0.11	0.14
$\leq C_2$	1.32	1.32	0.84	0.745	0.70	0.33	0.36
ΣC_3	6.40	6.68	6.24	4.86	4.03	2.45	2.20
ΣC_4	15.1	15.3	12.2	10.6	9.21	4.94	4.80
ΣC_5	9.22	9.45	7.59	6.04	5.49	3.74	3.54
C_5+ gasoline	60.0	57.9	60.6	60.4	56.5	42.0	35.2
C_6+ gasoline	50.8	48.4	53.0	54.4	51.0	38.3	31.7
LCO (TBP)	11.2	12.7	14.2	17.4	18.8	21.0	18.5
DO (TBP)	2.93	3.20	4.10	4.54	9.36	28.4	38.5
Coke	3.03	2.89	1.84	1.45	1.41	0.85	0.42
Conversion	85.9	84.1	81.7	78.1	71.9	50.6	43.0
C_6+ gasoline/Conversion	0.591	0.576	0.649	0.697	0.709	0.757	0.737
Coke/Conversion	0.0353	0.0344	0.0225	0.0186	0.0196	0.0168	0.0098
C_6+ gasoline/coke	16.7	16.7	28.8	37.5	36.2	45.1	75.2

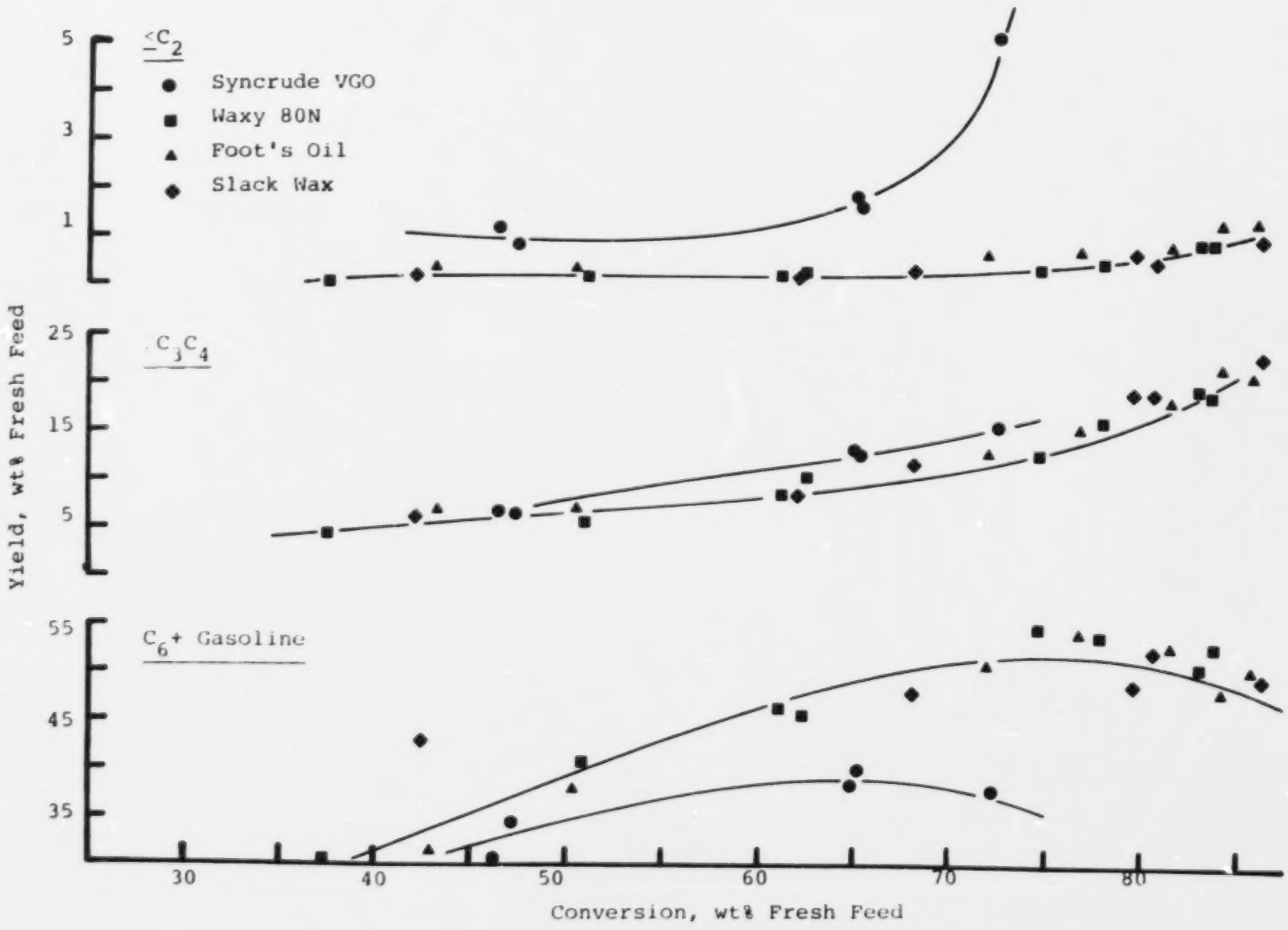
TABLE 13.6

MAT Product Yield Data for Slack Wax and Davison Super DX

Test	MAT 139	MAT 142	MAT 141	MAT 159	MAT 175	MAT 164
Mass Balance, wt%	103.4	104.2	100.0	100.7	100.0	97.2
T, °C	448.1	452.5	452.9	420.2	422.6	417.4
C/O, g/g	7.42	3.87	3.74	3.86	2.05	1.07
Yields, wt% FF						
H_2	0.01	0.00	0.00	0.00	0.00	0.00
CH_4	0.27	0.14	0.16	0.07	0.05	0.04
H_2S	0.00	0.00	0.00	0.04	0.00	0.05
ΣC_2	1.11	0.60	0.71	0.40	0.28	0.20
ΣC_3	6.95	6.52	6.27	3.73	2.90	2.22
ΣC_4	16.1	12.4	13.0	8.61	5.78	4.40
ΣC_5	9.61	7.74	8.94	5.70	4.30	3.40
C_5+ gasoline	59.3	60.3	58.0	53.7	47.7	34.9
C_6+ gasoline	49.7	52.6	49.1	48.0	43.4	31.5
LCO (220-344°C)	10.8	14.1	14.6	18.5	19.8	19.2
DO (344°C+)	2.79	5.42	5.85	13.7	22.6	38.8
Coke	2.90	1.63	1.54	1.39	0.90	0.34
Conversion, wt.% FF	86.4	80.5	79.6	67.9	62.0	42.0
C_6+ gasoline/Conversion	0.575	0.653	0.617	0.707	0.700	0.750
Coke/Conversion	0.0336	0.0202	0.0193	0.0204	0.0145	0.0081
C_6+ gasoline/coke	17.1	32.3	32.0	34.7	48.3	92.6

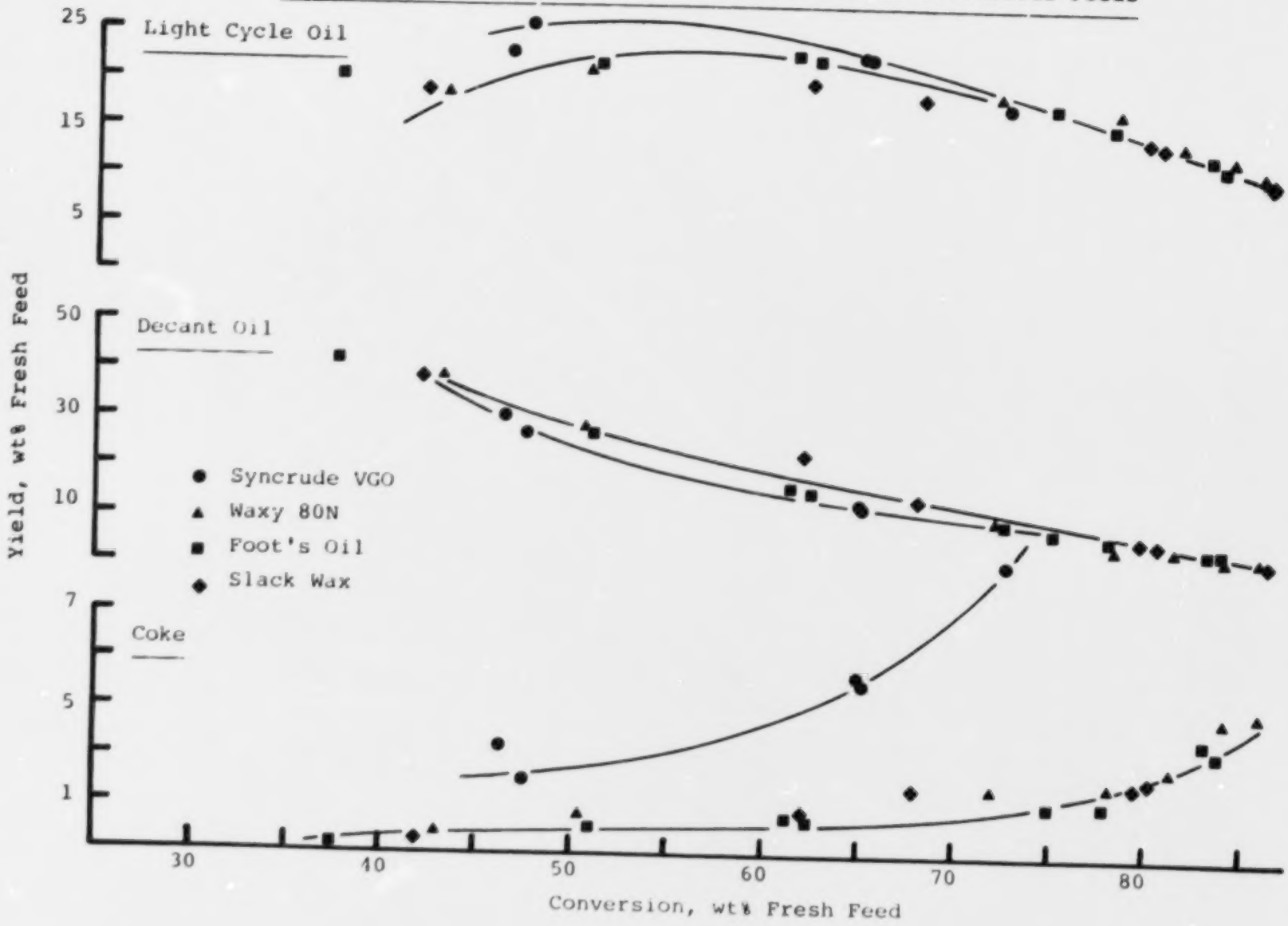
FIGURE 13.1

The Effect of Conversion on MAT Product Yields of Various Feeds



(Continued)

The Effect of Conversion on MAT Product Yields of Various Feeds



14) THE USE OF METAL PASSIVATORS

Additives such as antimony oxide (Sb_2O_3) have been added to FCCU feedstocks to passivate metals which are laid down on the cracking catalyst. This allows greater metals loading on the catalyst, extending its activity and reducing the catalyst makeup rate. Antimony in both inorganic and organic forms has been used when processing residua [12], although the former is preferred since it is easier to handle. Antimony is thought to act on nickel impurities and reduce their tendency to form coke as well as maintaining catalyst activity. Addition rates of 50% of the nickel added by weight are recommended. Antimony has no effect at all on vanadium impurities which attack the zeolite matrix. As a follow-up to our studies on metal impregnation, catalysts have been coimpregnated with nickel octoate, vanadium naphthenate and Nalco 500, a 22% Sb_2O_3 slurry in petroleum solvent. The catalysts so impregnated were equilibrium Super DX and DA-300 and they were evaluated by MAT testing with both IPL VGO and IPL 33.7 wt.% VTB/66.3 wt.% VGO at 490°C and three C/O ratios.

MAT product yield data for equilibrium Super DX, impregnated with approximately 1000 ppm Ni/V and 500 ppm Sb, and IPL VGO and VTB/VGO mixture are listed in Table 14.1. The effect of C/O on conversion for metals and antimony impregnated Super DX as well as metals impregnated and the equilibrium Super DX are shown graphically in Figure 14.1. Both the metals and antimony-impregnated Super DX and the equilibrium Super DX have similar conversions at equivalent C/O ratios. The metals impregnated Super DX had 7.5 to 10 wt.% lower conversions over the same range of C/O ratios. It is clear that antimony prevents any loss of conversion due to metals impregnation. Coke yields for these catalysts and IPL VGO, however, show much different trends (Figure 14.2). The metals and antimony impregnated catalyst has the largest coke yields at a given C/O while metals impregnated Super DX and equilibrium Super DX has successively lower coke yields. These yields can be expressed by the following relationships:

Impregnation	
1000 Ni/V, 500 Sb	coke yield (wt.%) = 1.655 (C/O) - 0.993
1000 Ni/V	coke yield (wt.%) = 1.007 (C/O) - 0.201
equilibrium	coke yield (wt.%) = 0.9091 (C/O) - 0.773

Similar results were also obtained with metals and metals and antimony impregnated Super DX and the residual feed IPL 33.7 wt.% VTB/66.3 wt.% VGO. Conversions for the antimony containing impregnated catalyst are 5-6 wt.% greater than for the metals impregnated catalyst (Figure 14.3). These results are directionally the same as those observed for IPL VGO but not as large. Coke yields for impregnated Super DX catalysts and IPL VTB/VGO are also larger for the antimony "passivated" catalysts. Coke yields for IPL VTB/VGO can be expressed as:

Impregnation	
1000 Ni/V, 500 Sb	coke yield (wt.%) = 2.381 (C/O) - 0.191
1000 Ni/V	coke yield (wt.%) = 1.763 (C/O) + 0.262

It is interesting to note that the difference in slope between these two relationships is very similar to the differences in slope for similar relationships determined for IPL VGO. Therefore, the slope of the coke/(C/O) relationship is a function of feedstock, catalyst and catalyst contamination. The troublesome point that arises with the above data is the explanation of the higher coke yields with antimony impregnation. It could be due to the Super DX catalyst which is a normal gas oil catalyst, or the method of impregnation.

Equilibrium DA-300 was also impregnated with 1000 ppm Ni/V and 500 ppm Sb. The impregnated catalyst was then evaluated in the microactivity test apparatus with both IPL VGO and VTB/VGO feeds. MAT product yields for these tests, done at 490°C and 3 C/O ratios, are listed in Table 14.2.

Conversion data as a function of C/O ratio for IPL VGO is shown for equilibrium, metals-impregnated (Ni/V) and metals- and antimony-impregnated DA-300 in Figure 14.5. The equilibrium and metals- and antimony-impregnated catalysts have similar conversions over the C/O range studied. The metals-impregnated catalyst has a depressed conversion of ~5 wt.% over the same C/O range. This again illustrates that antimony addition prevents a loss in catalyst activity with metal-(Ni/V) impregnation. Unfortunately, coke response to C/O ratio for these DA-300 catalysts is similar to that experienced for Super DX catalyst with IPL VGO. Results in Figure 14.6 show that with IPL VGO both metals (Ni/V) and metals- and antimony-impregnated DA-300 have similar and large

coke yields relative to equilibrium DA-300. These yields can be expressed by the following linear equations:

Impregnation	
1000 Ni/V, 500 Sb	coke yield (wt.%) = 2.116 (C/O) - 1.800
1000 Ni/V	coke yield (wt.%) = 1.695 (C/O) - 0.339
equilibrium	coke yield (wt.%) = 1.121 (C/O) - 0.354

These results again indicate that antimony has no effect on reducing the coke-forming tendencies of metal contaminants.

Conversion, C/O data were also evaluated for IPL 33.7% VTB/ 66.3% VGO and the three types of DA-300 catalysts (equilibrium, metals-impregnated, metals- and antimony-impregnated). Conversions are greatest for the equilibrium catalyst and successively 2.5 wt.% less for metals- and antimony-impregnated catalyst and metals-impregnated catalyst for $2 \leq C/O \leq 7$ (Figure 14.7). Coke yields as a function of C/O (Figure 14.8) return to the pattern established with IPL VGO and these catalysts. The metals- and antimony-impregnated catalyst gives high coke yields relative to the equilibrium catalyst but these yields are similar to those of the metals impregnated catalyst. The coke yields correlate as follows:

Impregnation	
1000 Ni/V, 500 Sb	coke yield (wt.%) = 2.791 (C/O) - 0.116
1000 Ni/V	coke yield (wt.%) = 2.281 (C/O) + 2.552
equilibrium	coke yield (wt.%) = 2.105 (C/O) - 0.642

These results again imply that antimony does not affect coke response, which is not valid, and therefore the method of impregnation is suspect.

Since the method of impregnation was suspect, it was decided to evaluate other methods of metals- and antimony-impregnation. Our supply of equilibrium DA-300 had been exhausted so equilibrium GRZ-1, studied previously with IPL VGO, was used as the starting material for impregnation studies. Four methods of impregnation were employed to place approximately 1000 ppm Ni/V and 500 ppm Sb on the catalyst. These included, 1) impregnation with nickel and vanadium soaps and an Sb_2O_3 suspension (Nalco N-5000) followed by 8 h exposure to steam and air at 1350°F, 2) impregnation as above,

followed by coking the catalyst with gas oil and then steaming the coked residue with air at 1350°F, 3) as in 1) except triphenylstilbene, an organoantimony compound, was used, and 4) as in 2) except triphenylstilbene employed. The catalysts after steaming were collected and stored in a desiccator. Elemental analyses for Ni, V, Fe and C are listed in Table 14.3 and show that the impregnated catalysts are compositionally quite similar.

Microactivity tests for the four impregnated catalysts were carried out with IPL VGO at 490°C and three C/O ratios. Results for these tests are listed in Table 14.4 along with data for equilibrium GRZ-1.

A comparison of conversion vs. C/O data for the four impregnated catalysts and equilibrium GRZ-1 can be found in Figure 14.9. The data show that no impregnated catalyst has the same activity as the base case equilibrium catalyst. Catalyst from preparation 4) has conversions similar to that of equilibrium catalyst as low C/O ratios and catalyst from preparation 2) appears as active at C/O 4. However, over the range of C/O, no impregnated catalyst is as active as equilibrium catalyst. Preparations 3) and 2) produce impregnated catalysts which give notably lower conversions. Therefore, from a conversion standpoint the method of impregnation appears very important.

The effect of C/O on coke yield is remarkably similar for all impregnated catalysts and the base case equilibrium catalyst (Figure 14.10):

impregnated GRZ-1 catalysts	coke yield (wt.%) = 1.899 (C/O) - 0.766
equilibrium GRZ-1	coke yield (wt.%) = 1.849 (C/O) - 1.44

These results are opposite to those obtained with DA-300 and may be due to the differences in metals levels on the equilibrium catalysts. However, to substantiate this, more work at various levels of impregnation is required.

TABLE 14.1

MAT Product Yield Data for IPL VGO and 33.7% VTB/66.3% VGO with Impregnated Super DX

Test	MAT 572	MAT 573	MAT 594	MAT 569	MAT 570	MAT 571
Mass Balance, wt%	96.1	101.6	100.3	98.9	100.6	96.6
Feed	VGO	VGO	VGO	VTB/VGO	VTB/VGO	VTB/VGO
Metals Levels						
Ni, ppm	1154	1154	1154	1154	1154	1154
V, ppm	1400	1400	1400	1400	1400	1400
Sb, ppm	482	482	482	482	482	482
T, °C	489	491	491	490	490	490
C/O, g/g	1.86	3.57	6.07	2.25	4.55	5.98
Product Yields, wt%						
H_2	0.34	0.51	0.83	0.55	0.96	1.22
CH_4	0.29	0.43	0.84	0.82	1.20	1.44
$\leq C_2$	1.15	1.70	3.00	2.56	3.87	4.75
ΣC_3	4.35	4.36	5.83	4.18	6.51	7.64
ΣC_4	8.28	7.93	10.6	6.96	11.1	13.8
ΣC_5	5.87	4.23	7.85	4.75	7.94	9.57
C_5^+ gasoline	35.7	47.1	47.8	37.5	44.2	41.0
C_6^+ gasoline	29.9	42.8	39.9	32.5	36.2	31.4
LCO	19.7	20.5	15.1	19.9	15.5	12.4
DO	28.5	13.7	8.40	23.5	8.34	6.02
Coke	2.32	4.74	9.31	5.39	10.4	14.4
Conversion	51.9	65.8	76.5	56.6	76.1	81.5
C_6^+ gasoline/Conversion	0.576	0.650	0.522	0.578	0.476	0.385
Coke/Conversion	0.045	0.072	0.122	0.095	0.137	0.177
C_6^+ gasoline/coke	12.8	9.03	4.28	6.08	3.47	2.18

FIGURE 14.1

The Effect of C/O Ratio on Conversion for Passivated Metals Impregnated Super DX and IPL VGO

T = 490°C

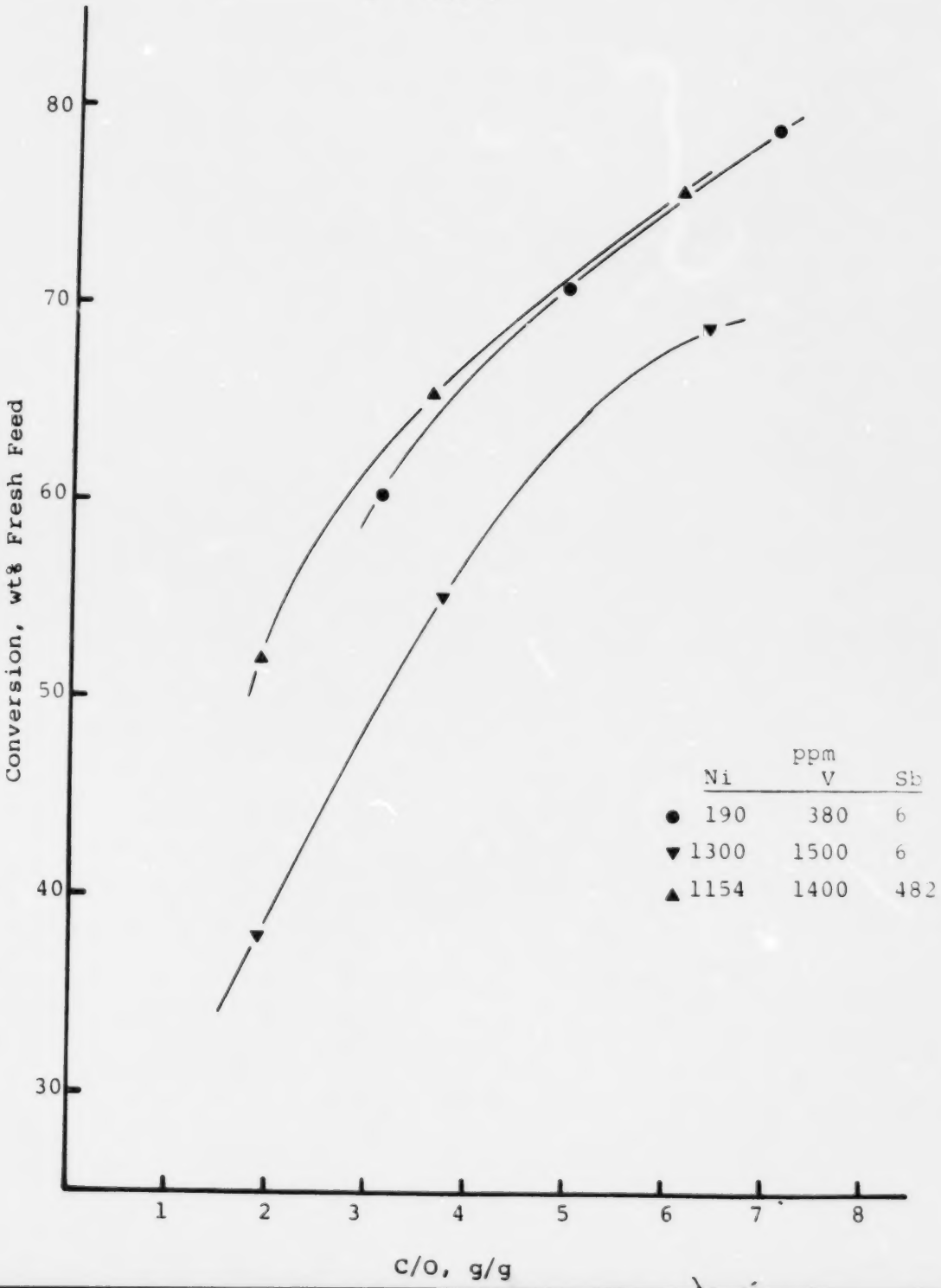


FIGURE 14.2

The Dependence of Coke Yield on C/O Ratio for Passivated Metals Impregnated Super DX and IPL VGO

T = 490°C

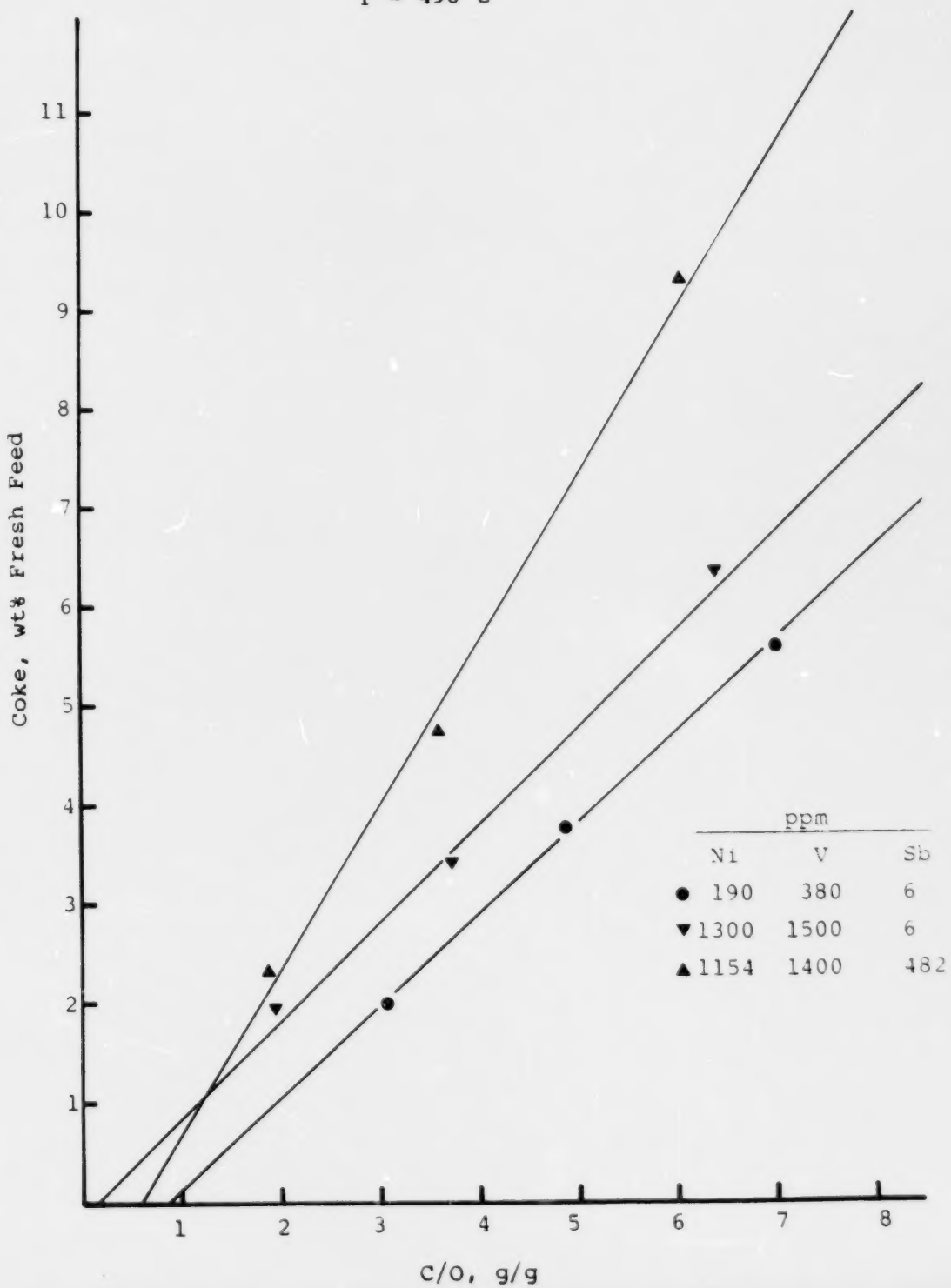


FIGURE 14.3

The Effect of C/O Ratio on Conversion for Passivated Metals Impregnated Super DX and IPL 33.7% VTB/66.3% VGO

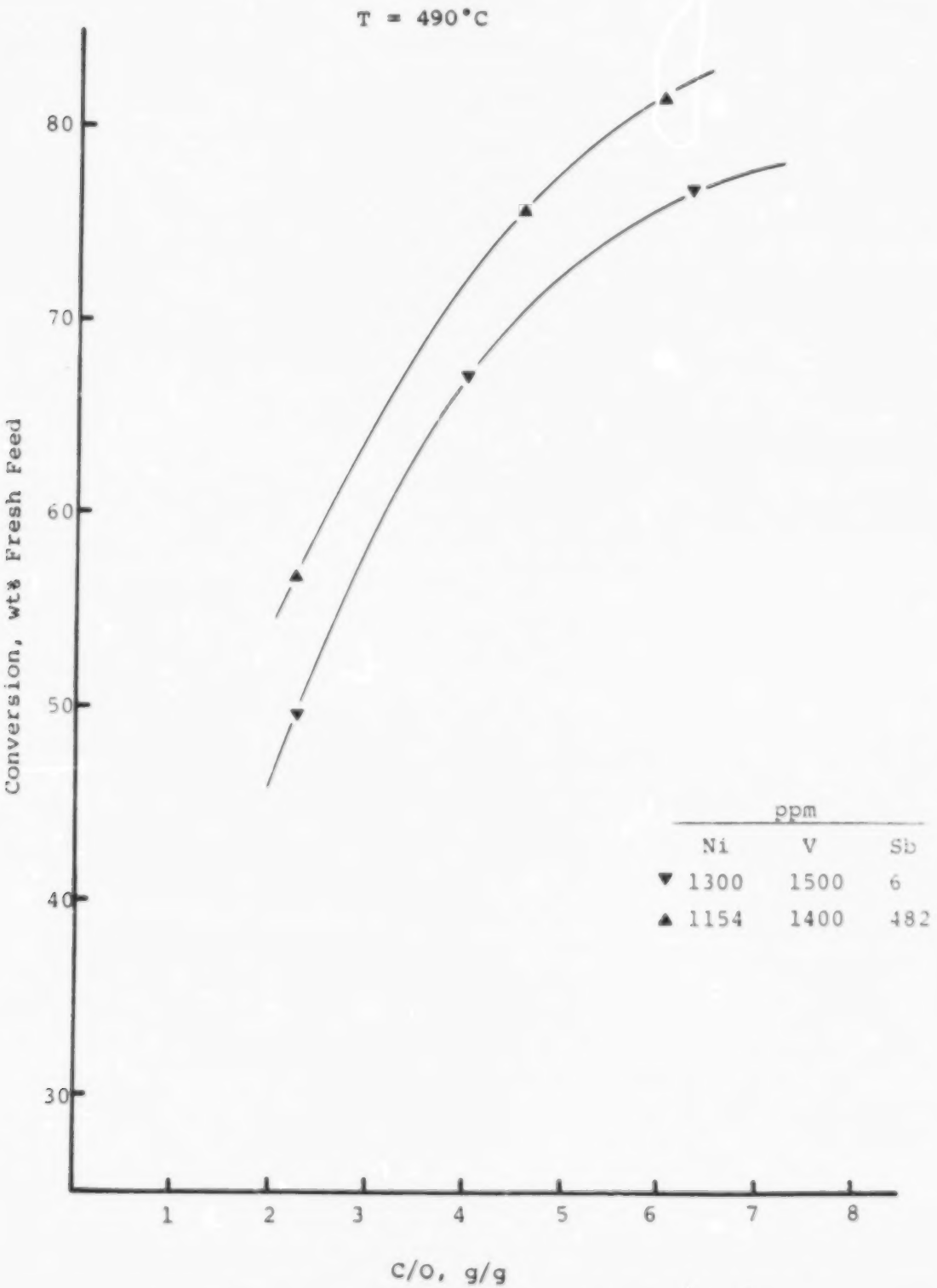


FIGURE 14.4

The Dependence of Coke Yield on C/O Ratio for Passivated Metals Impregnated Super DX and IPL 33.7% VTB/66.7% VGO

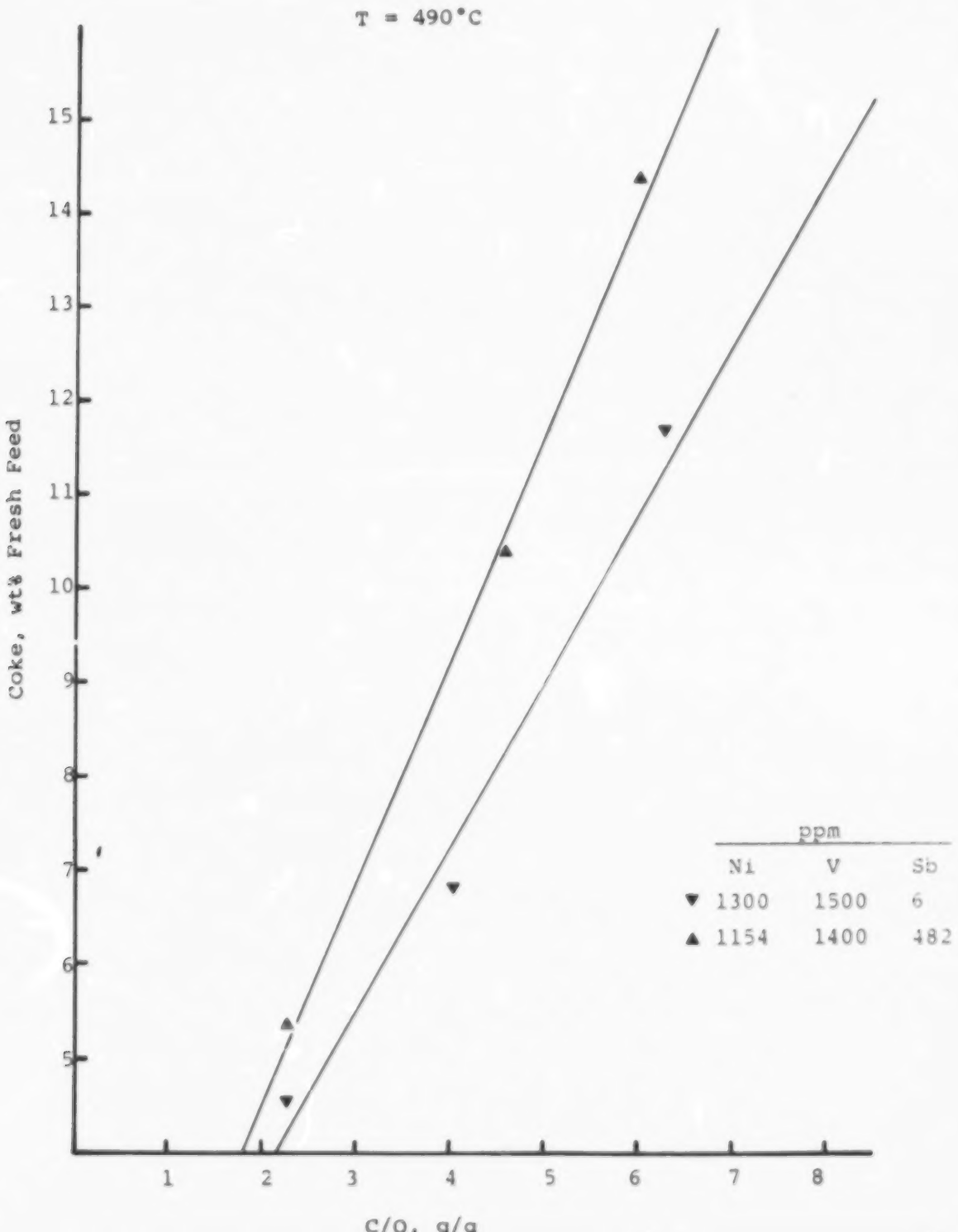


TABLE 14.2

MAT Product Yield Data for IPL VGO and 33.7% VTB/66.3% VGO with Impregnated DA-300

Test	MAT 577	MAT 575	MAT 576	MAT 578	MAT 579	MAT 580
Mass Balance, wt%	100.9	97.4	96.8	97.3	102.5	103.7
Feed	VGO	VGO	VGO	VTB/VGO	VTB/VGO	VTB/VGO
Metals Levels						
Ni, ppm	1584	1584	1584	1584	1584	1584
V, ppm	3899	3899	3899	3899	3899	3899
Sb, ppm	600	600	600	600	600	600
T, °C	490	490	489	490	490	489
C/O, g/g	2.19	3.84	5.26	2.26	3.59	6.62
Product Yields, wt%						
H_2	0.46	0.96	1.55	0.77	0.99	1.57
CH_4	0.28	0.66	1.21	0.85	1.11	1.67
ΣC_2	1.23	2.68	4.41	2.78	3.58	5.39
ΣC_3	3.30	6.14	8.17	4.93	6.01	7.47
ΣC_4	6.01	11.6	14.6	8.34	10.3	12.9
ΣC_5	3.23	6.54	8.63	4.92	6.56	8.69
C_5^+ gasoline	37.0	42.9	41.2	38.6	42.5	36.7
C_6^+ gasoline	33.7	36.4	32.5	33.7	36.0	28.0
LCO	22.6	18.6	14.2	20.5	17.9	12.4
DO	26.7	12.3	7.51	18.5	10.0	6.02
Coke	3.18	5.89	9.91	6.32	9.60	19.1
Conversion	50.7	69.2	78.2	61.0	72.1	81.5
C_6^+ gasoline/Conversion	0.665	0.526	0.416	0.552	0.499	0.344
Coke/Conversion	0.063	0.085	0.127	0.268	0.1233	0.234
C_6^+ gasoline/coke	10.6	6.19	3.28	2.08	3.75	1.47

FIGURE 14.5

The Effect of C/O Ratio on Conversion for Passivated Metals Impregnated DA-300 and IPL VGO

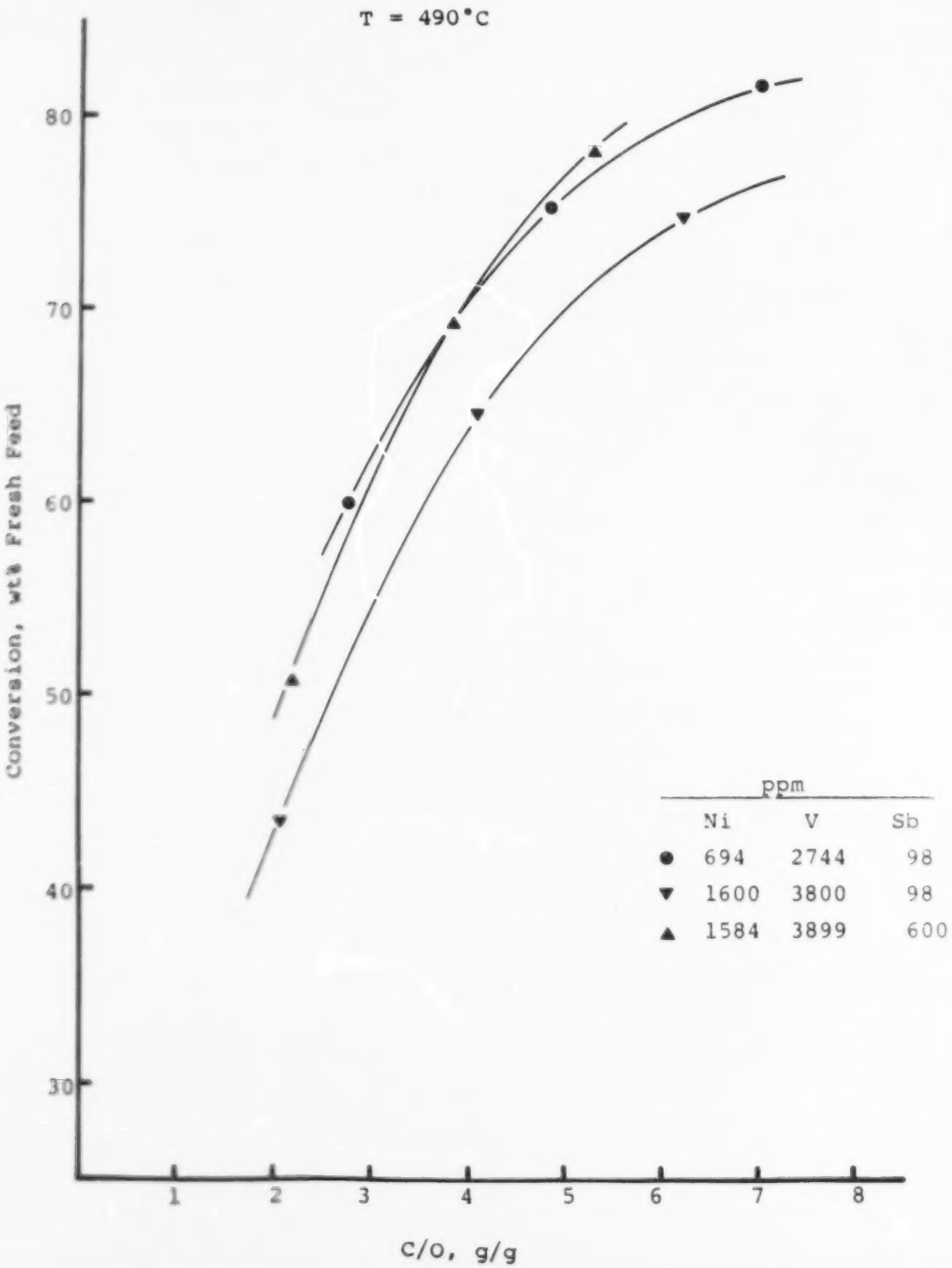


FIGURE 14.6

The Dependence of Coke Yield on C/O Ratio for Passivated Metals Impregnated DA-300 and IPL VGO

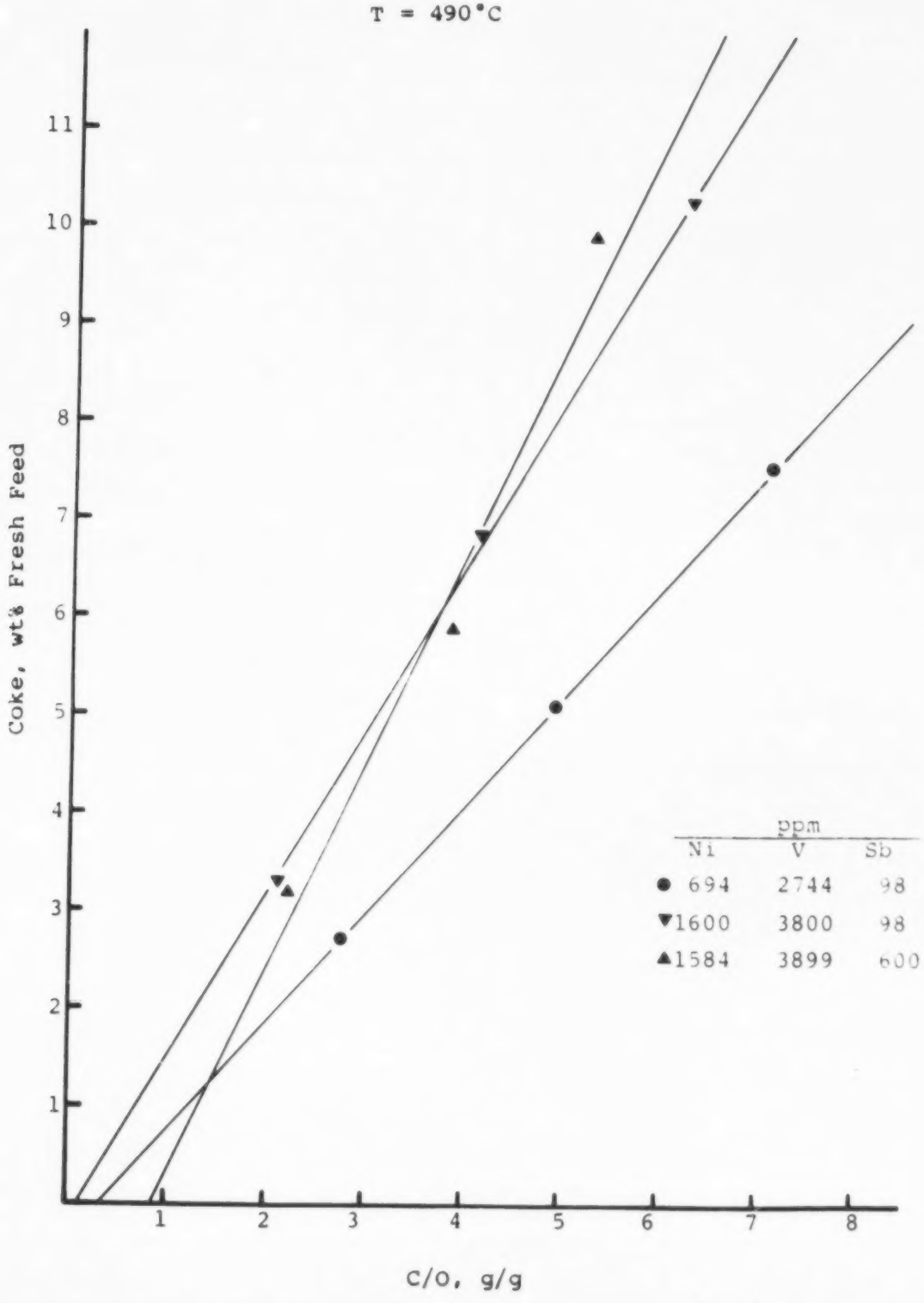


FIGURE 14.7

The Effect of C/O Ratio on Conversion for Passivated Metals Impregnated DA-300 and IPL 33.7% VTB/66.3% VGO

T = 490°C

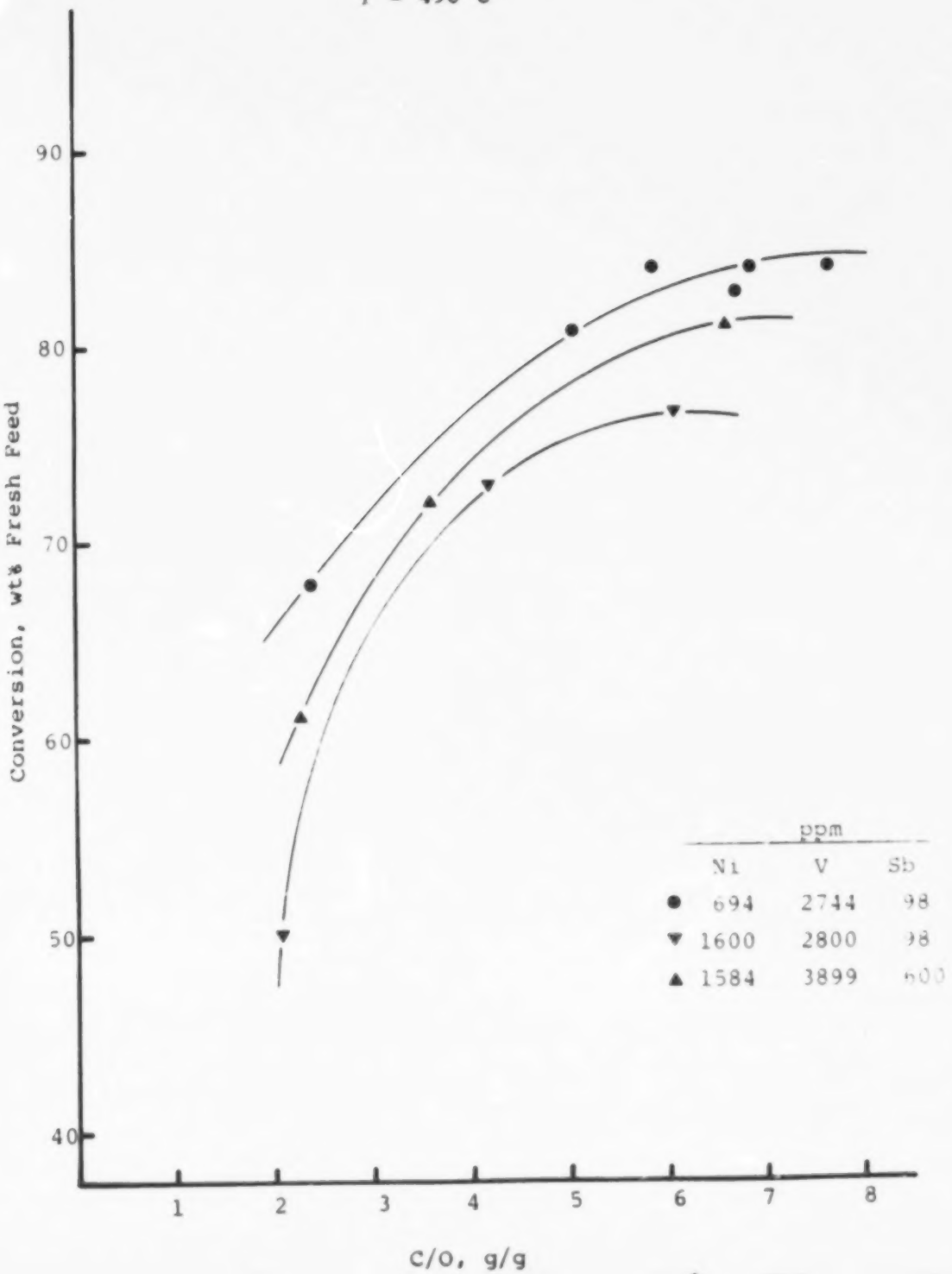


FIGURE 14.8

The Dependence of Coke Yield on C/O Ratio for Passivated Metals Impregnated DA-300 and IPL 33.7% VTB/66.3% VGO

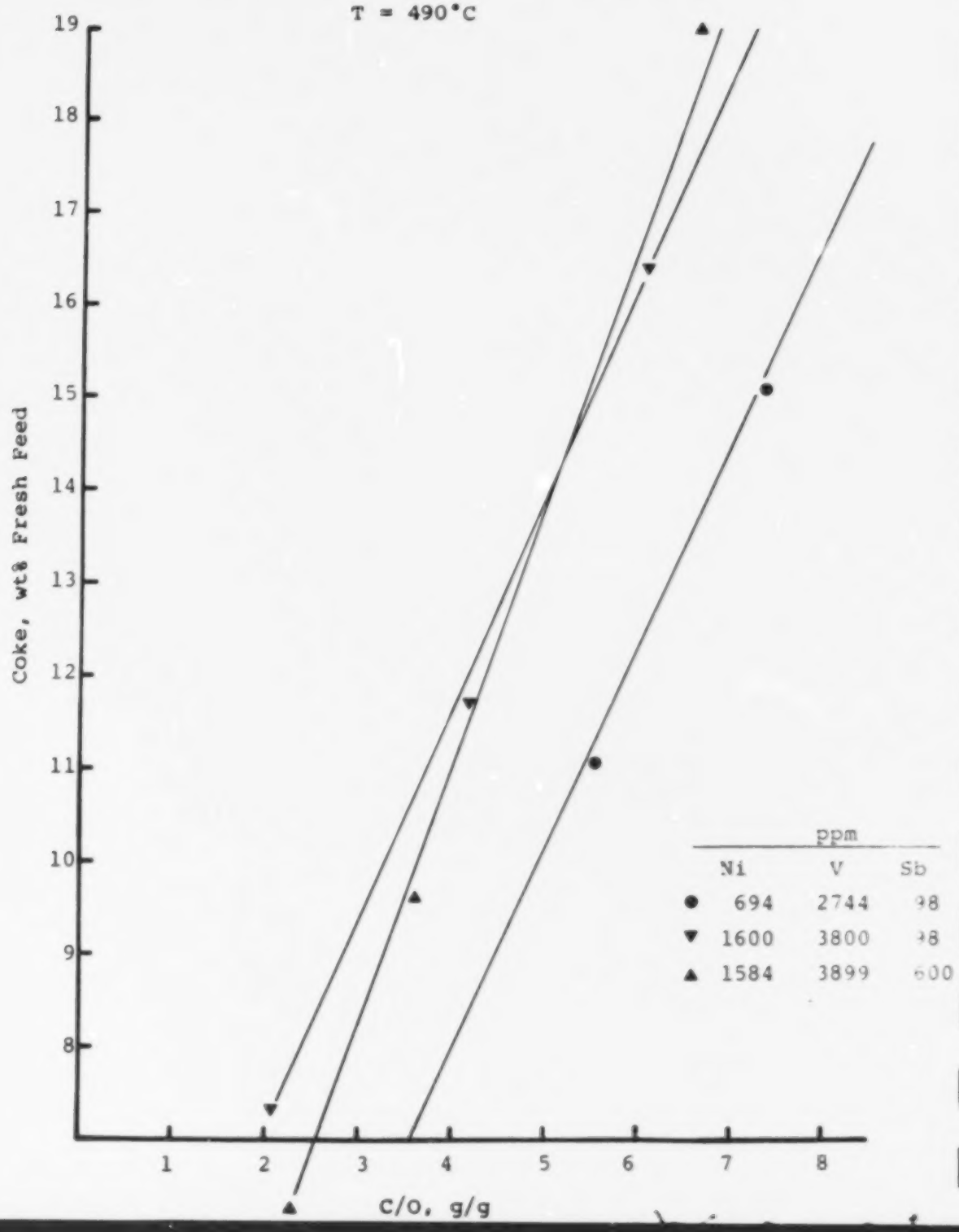


TABLE 14.3

Metals Contents of Impregnated Equilibrium GRZ-1 Catalyst
(Attempted Level of Impregnation: 1000 ppm Ni, 1000 ppm V, 500 ppm Sb)

Method of Impregnation	None	1	2	3	4
Metals Content, ppm					
Fe	10,900	10,800	11,100	10,500	11,700
Ni	678	1,510	1,380	1,480	1,500
V	950	1,040	1,910	1,960	1,950
Sb	8	630	460	600	520
Wt%, C	0.23	0.04	0.03	0.02	0.03

1. Sb_2O_3, oxidation with steam at 1350°F
2. Sb_2O_3, coked with gas oil then oxidation with steam at 1350°F
3. $Sb\emptyset_3$, oxidation with steam at 1350°F
4. $Sb\emptyset_3$, coked with gas oil then oxidation with steam at 1350°F

TABLE 14.4

MAT Product Yield Data for IPL Vacuum Gas Oil and Impregnated GRZ-1

Test	MAT 322	MAT 323	MAT 324	MAT 589	MAT 590	MAT 591	MAT 592	MAT 593	MAT 594
Mass Balance, wt%	100.3	102.4	102.6	101.5	100.0	103.8	102.7	101.5	99.9
Catalyst Preparation	———	None	———	———	1	———	———	2	———
Metal Levels (ppm)									
Ni	———	678	———	———	1510	———	———	1380	———
V	———	950	———	———	2040	———	———	1910	———
Sb	———	8	———	———	630	———	———	460	———
T, °C	490	490	489	491	489	491	490	490	491
C/O, g/g	2.63	2.54	6.67	1.92	3.66	5.80	2.06	4.33	6.97
Product Yields, wt%									
H_2	0.09	0.16	0.30	0.29	0.67	0.69	0.29	0.48	0.98
CH_4	0.50	0.97	2.09	0.28	0.64	0.66	0.30	0.51	1.21
$\leqslant C_2$	1.80	3.11	5.57	1.15	2.47	2.53	1.18	1.85	3.87
ΣC_3	5.50	7.48	9.90	3.56	5.97	6.11	3.61	4.73	7.16
ΣC_4	10.2	13.9	17.2	6.87	11.6	11.8	7.14	9.09	13.3
ΣC_5	5.28	7.45	9.92	4.01	8.04	8.22	4.52	6.57	9.54
C_5+ gasoline	44.3	46.0	41.3	38.2	45.5	44.7	39.9	47.5	43.9
C_6+ gasoline	39.0	38.5	31.3	34.2	37.8	36.5	35.4	41.0	34.4
LCO	13.9	11.9	9.85	16.1	14.1	14.2	16.7	15.7	12.4
DO	20.7	10.8	5.06	31.0	14.6	10.3	28.2	13.6	6.58
Coke	3.54	6.87	11.1	3.05	5.80	10.3	3.24	7.5	12.8
Conversion	65.4	77.4	85.1	52.8	71.4	75.4	55.1	70.7	81.0
C_6+ gasoline/Conversion	0.596	0.497	0.368	0.648	0.529	0.484	0.642	0.580	0.435
Coke/Conversion	0.054	0.089	0.130	0.058	0.081	0.137	0.059	0.106	0.158
C_6+ gasoline/coke	11.0	5.60	2.82	11.2	6.51	3.54	10.9	5.47	2.69

TABLE 14.4(Cont'd)

MAT Product Yield Data for IPL Vacuum Gas Oil and Impregnated GRZ-1

Test	MAT 595	MAT 596	MAT 597	MAT 598	MAT 599	MAT 600
Mass Balance, wt%	102.6	100.7	99.9	101.7	103.6	
Catalyst Preparation	3			4		
Metal Levels (ppm)						
Ni	1480			1500		
V	1460			1950		
Sb	600			520		
T, °C	490	489	490	490	490	490
C/O, g/g	1.89	4.13	6.18	2.11	3.53	7.98
Product Yields, wt%						
H_2	0.19	0.34	0.52	0.28	0.48	0.82
CH_4	0.30	0.55	0.92	0.35	0.65	1.29
$\leq C_2$	1.06	1.81	2.80	1.29	2.17	3.91
ΣC_3	3.78	5.51	6.75	4.34	5.76	7.67
ΣC_4	7.34	10.9	13.0	8.41	11.1	14.7
ΣC_5	4.71	7.71	8.46	5.27	6.42	10.7
C_5+ gasoline	41.4	46.7	47.3	42.4	46.6	43.6
C_6+ gasoline	36.7	39.0	38.8	37.1	40.2	33.0
LCO	16.1	14.7	12.6	15.9	14.7	11.5
DO	27.5	13.8	7.37	24.2	13.4	6.13
Coke	2.76	6.55	10.1	3.47	6.25	12.4
Conversion	56.4	71.5	80.0	59.9	72.0	82.3
C_6+ gasoline/Conversion	0.651	0.545	0.485	0.619	0.558	0.401
Coke/Conversion	0.049	0.092	0.126	0.058	0.087	0.151
C_6+ gasoline/coke	13.3	5.95	3.84	10.7	6.43	2.66

FIGURE 14.9

The Effect of C/O Ratio on Conversion for Passivated Metals Impregnated GRZ-1

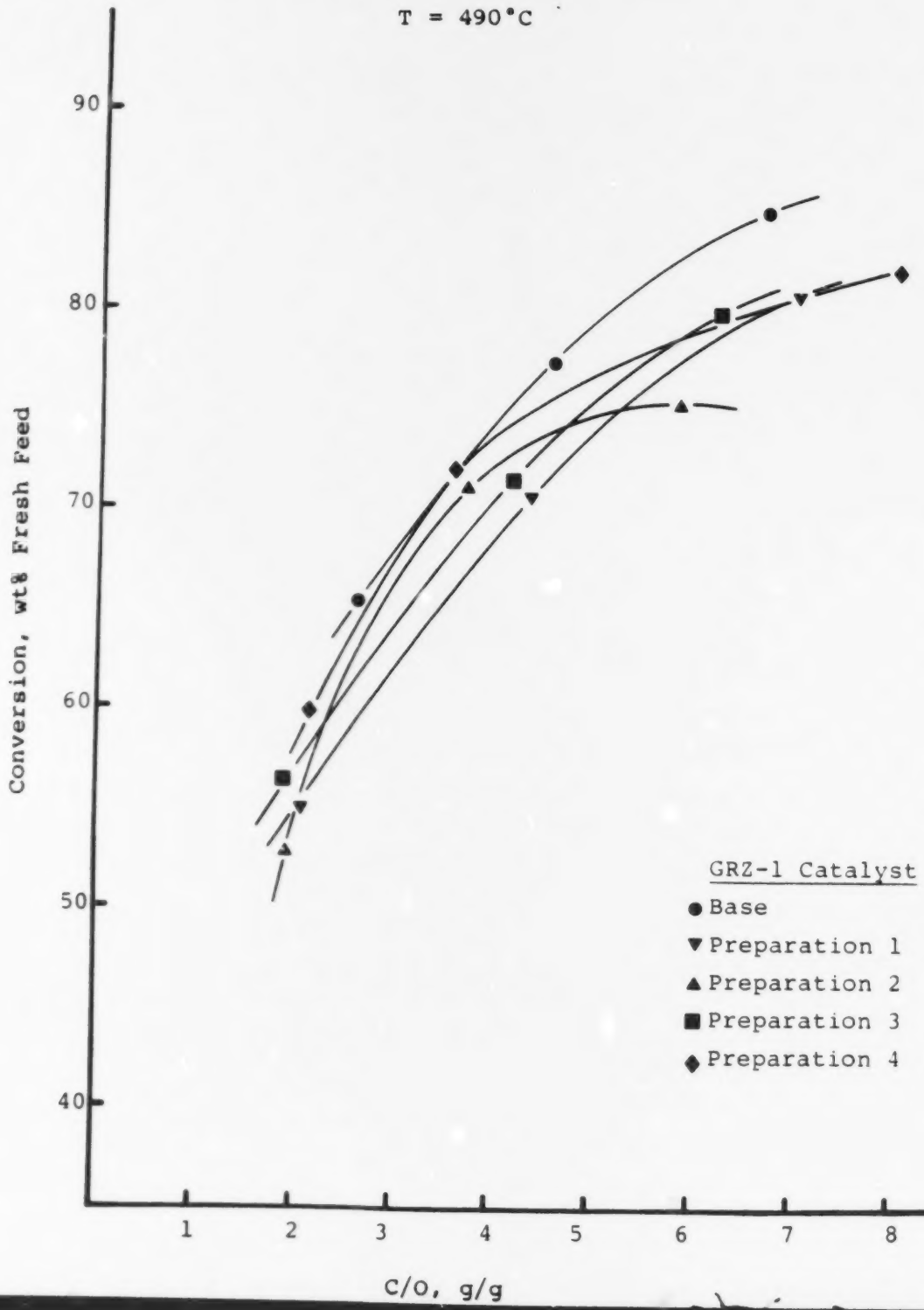
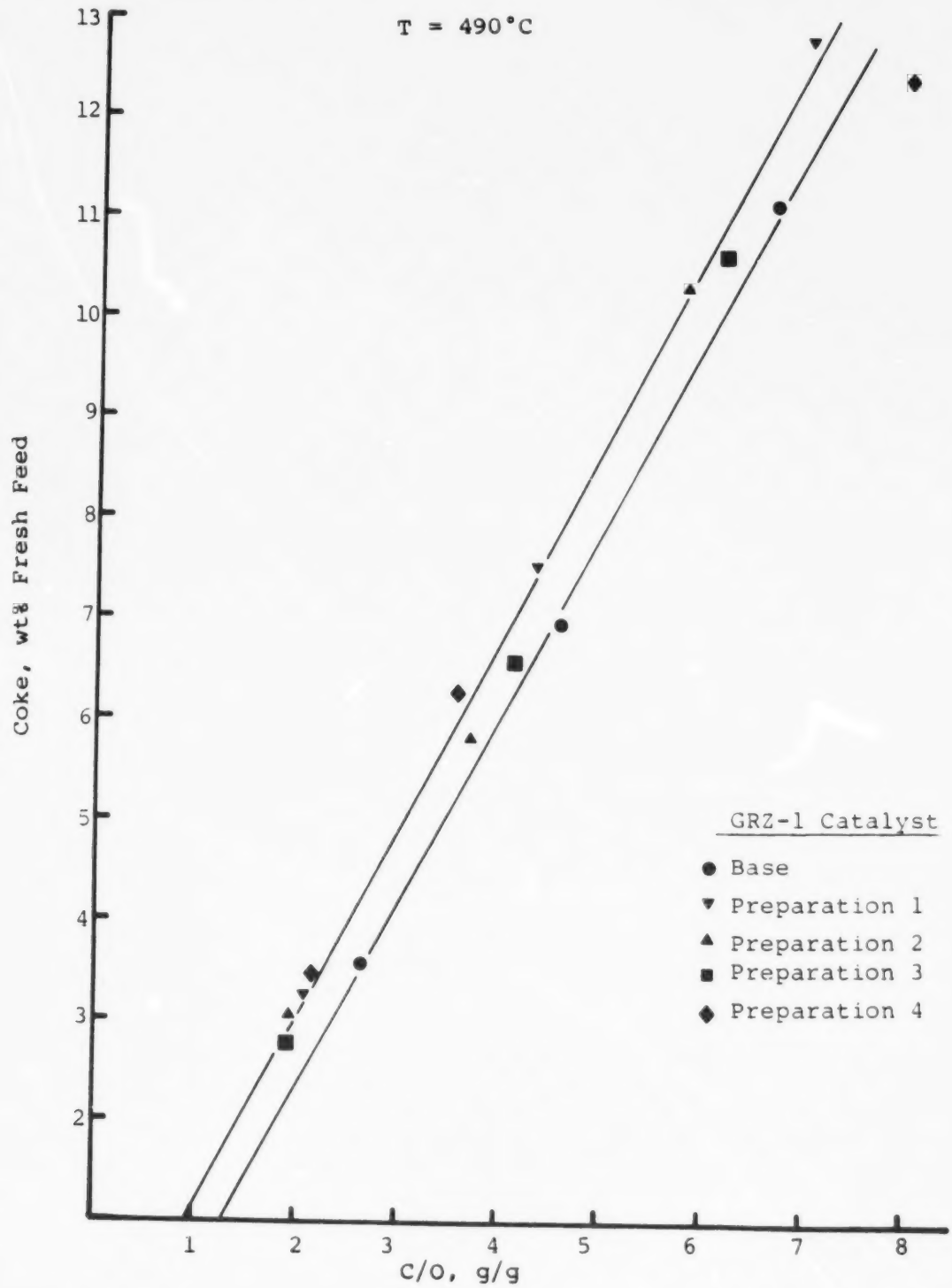


FIGURE 14.10

The Dependence of Coke Yield on C/O Ratio for Passivated Metals Impregnated GRZ-1



15) UTILITY OF THE DATA

A commercial FCCU unit and a MAT reactor vary in three major ways. The former is a thermally balanced unit where both feedstock cracking and catalyst regeneration occur, while the latter only accommodates the cracking reactions and is not thermally balanced. The commercial FCCU also has various recycle streams, while the MAT unit is operated on a once through basis. Finally, the riser in a commercial FCCU is an upward flowing, entrained bed, while the MAT contains a fixed bed of catalyst through which the feedstock and inert carrier gas flow downwards. If thermal balancing is ignored and the effect of recycle streams assumed constant, the differences in MAT and commercial yields can be assumed to differ by constant amounts which reflect mechanical differences in these units. As a result, a refiner can use the MAT data to model his own operation, provided he has commercial yield data with which MAT data can be correlated. Differences in MAT and commercial yields with the same feed and catalyst can be applied to MAT data with unknown feedstocks or catalysts, thereby developing an estimate of a commercial yield. This process can be applied several times with changes in feed, catalyst or other operating conditions to estimate desired commercial FCCU yield data. For the commercial unit, the commercial yield model must be evaluated for heat balance and regenerator temperature as outlined in the literature [13, 14] and Appendix 1 or as calculated by proprietary models.

CONCLUSIONS

1. Of the equilibrium catalysts evaluated with IPL vacuum gas oil, Super DX was shown to be more selective for gasoline and less selective for coke than either DA-300 or GRZ-1. The latter catalysts were contaminated with a high level of metals (Ni and V) and had very high activity, respectively. Unfortunately, Super DX cannot tolerate residuum cracking conditions due to a low metals tolerance.

2 IPL, Lloydminster and Syncrude vacuum gas oils were evaluated as cracking feedstocks with DA-300. IPL VGO was the superior feedstock producing much more gasoline than Lloydminster VGO, which in turn was only marginally better than Syncrude VGO.

3. Relative to their respective vacuum gas oils, residua produced more coke, light ends, LPGs and light cycle oil and less gasoline and decant oil per unit weight of feed at similar conversions.

4. The overall yield of potential liquid products (LPGs, C_5+ gasoline and light cycle oil) was somewhat less for residua than for conventional gas oils. The quality of cracked residua products, however, has not been determined but was anticipated to be poorer.

5. Residua like gas oils have shown variable quality as FCCU feedstocks. Quality is dependent upon composition and detrimental catalyst contaminants such as nickel and vanadium compounds.

6. Metals (Ni & V) contamination of Super DX and DA-300 catalysts adversely affected catalyst activities and increased the level of coke laid down on the catalysts.

7. Coimpregnation of DA-300 and Super DX with antimony as well as nickel and vanadium soaps showed that the antimony compound prevented losses in catalyst activity, but did not reduce the coke forming tendency of the catalyst. Maintenance of activity and reduction of coke due to metals was expected; therefore, the method of impregnation was suspect and should be evaluated further.

8. Impregnation of GRZ-1 catalyst with nickel and vanadium soaps as well as Sb_2O_3 or triphenylstilbene under both oxidizing and reducing then oxidizing conditions, met with mixed results. Conversions were generally lower but coke yields were only marginally greater. This was the reverse of what was observed with DA-300 and is likely due to the high activity of GRZ-1.

9. A comparison of gas oil feedstocks ranging in composition from aromatic Syncrude vacuum gas oil to cycloparaffinic and paraffinic materials shows that all saturate feeds produce similar large yields of liquid products. As a result, the saturation of Syncrude vacuum gas oil would be sufficient to produce an excellent FCCU feed.

RECOMMENDATIONS

1. Other methods for processing residua into FCCU feedstocks should be evaluated for comparison. These methods include, 1) residua solvent deasphalting where metals and coke precursors can be rejected and a heavy but compositionally good quality feed produced, and 2) hydrogenation of the residua to remove metals and coke precursors, thus improving feedstock quality.

2) Detailed compositional characterization on the above feeds should be undertaken so that composition and cracking yields can be correlated.

3) MAT data should be extended to evaluate product quality. This would require the development of microanalytical methods to determine gasoline and light cycle oil quality in the MAT reactor effluent liquid.

4) More effective methods for the evaluation of catalyst activity and degradation should be developed. In this work we have shown the strong correlation between product yield and composition. Perhaps the use of model compounds or molecular probes may lead to a better understanding of the catalytic processes which occur on the catalyst as cracking reactions occur.

ACKNOWLEDGEMENTS

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APPENDIX 1

CALCULATION OF FCCU REGENERATOR TEMPERATURES FROM MICROACTIVITY DATA

This FCCU regenerator temperature calculation is taken from a paper by Pierce [13].

Introduction

In a typical FCCU heat balance calculation, the following parameters are known:

1. Fresh and Total feed flows (Total Feed = Fresh Feed + Recycle)
2. Fresh and Total feed gravities
3. Flue gas composition
4. Air rate to regenerator
5. Reactor temperature
6. Regenerator bed and top temperatures
7. Air blower discharge temperature

The following parameters are calculated:

1. Coke make
2. Catalyst-to-oil ratio

In Microactivity (MAT) work, the following parameters are known:

1. Fresh feed gravity
2. Catalyst-to-oil ratio
3. Coke make

In this work, the desired parameter to be calculated was the regenerator bed temperature.

Assumptions

Because MAT work deals with only the reactor side of an FCCU, several assumptions had to be made about the operation of the regenerator which would be associated with the reactor, and also about the unit as a whole. The explanations are on the following pages.

1. Fresh feed rate = Total feed rate (no recycle)
2. Feed rate = 20 000 BPD
3. Actual reactor temperature is 100°F higher than MAT reactor temperature

4. MAT coke value is Carbon only (Hydrogen will be calculated)
5. Actual carbon value is MAT coke value + an experimentally determined delta value (in this case, delta = -1.66)
6. Datum temperature is 60°F
7. Heat losses from the flue gas and miscellaneous are calculated as 35 percent of the total heat to the regenerator
8. The air blower discharge temperature is 300°F
9. The flue gas composition (mole%) is: $CO_2/CO/O_2/SO_2/N_2$+Ar = 14.0/7.0/0.2/0.1/78.7 (CO_2:CO = 2.1)

The reasons for the assumptions are as follows:

1. Most commercial FCC units operate with some recycle of the heavy material in an attempt to reduce bunker yield and improve conversion. Therefore, in calculating a heat balance around the reactor-regenerator, the total combined feed flow and gravity must be known, as heat is involved in the movement and reaction of the recycle. A MAT unit, however, is a once-through system; estimating how much recycle there would be and how it would react in a MAT is beyond the scope of this task.

2. Since a commercial FCC unit is a continuous operation, some kind of feed rate must be given in order to calculate the carbon and hydrogen production rates, and therefore the rates of heat generation. The figure of 20 000 BPD was taken as representative of a medium-sized FCCU in a Canadian refinery.

3. In a commercial FCCU, the temperature of a riser-reactor is not an independent variable - among other things, it is dependent on the preheat temperature and the catalyst-to-oil ratio. In a MAT unit, while the cat-to-oil ratio and reactor temperature may be related, they can be set independently. Also, the MAT furnace just cannot operate at temperatures as high as an FCCU reactor. Experience with this MAT unit and commercial FCC units has shown that, for the same operating severity (same conversion, product slate and coke make) the unit reactor temperature is about 100°F higher than the MAT reactor temperature.

4. In a MAT, the coke yield is determined by analysing the spent catalyst for mass percent carbon. Hydrogen on catalyst is not determined, although it is part of coke production in a commercial unit. However, once the carbon value is known, the hydrogen value can be calculated from the stoichiometric equations.

5. The delta value between MAT coke make and commercial unit coke make has been determined experimentally.

6. The heat produced or lost is calculated based on the difference between the reactor or regenerator temperatures and a datum (ambient) temperature. For practical purposes, this datum temperature is usually 60°F.

7. Radiation and miscellaneous heat losses are generally assumed to be 6% of the total heat of combustion. Heat losses in the flue gas are usually calculated from the flue gas temperature and the flue gas rate. Since the flue gas composition was to be set as a constant fo the series of MAT runs, the heat loss for that composition was estimated to be about 30% of the total heat to the regenerator. The total heat losses were then set at 35% of the total heat to the regenerator.

8. Although the air rate can be calculated, the temperature of the air coming into the regenerator must be known. All air blowers are different, but a typical value was found to be 300°F. In addition, no air blower constraints were assumed, although the air blower constraint may well be a limiting factor in a commercial unit.

9. Selecting a flue gas composition was the most difficult task, as the accuracy of this composition is vital to the accuracy of the heat balance. Most commercial units tend to operate to a desired regenerator temperature and carbon on regenerated catalyst (CRC); the flue gas composition is related to these, the coke yield and the air rate by a series of complicated kinetic equations. The coke make can be calculated from the flue gas analysis, but the equations are not reversible. Therefore, the flue gas composition must be known. In general, once an FCC unit is in heat balance, very little can be done (short of changing the feedstock or the catalyst) to change either the reactor or the regenerator.

The flue gas composition was selected to be as representative as possible of a "typical" FCCU in heat balance operating on conventional gas oil. Although in a commercial unit flue gas composition will vary with feedstock and severity, in the MAT work the flue gas was held constant for comparison purposes.

STARTING VARIABLES FOR REGENERATOR TEMPERATURE CALCULATIONS

1. Feed rate: 20 000 BPD (assumption 2)
2. Reactor temperature: MAT temp + 100°F (assumption 3)
3. MAT coke make, mass% feed
4. Flue gas composition (assumption 9)
5. Datum or ambient temperature: 60°F (assumption 6)
6. Air blower discharge temperature: 300°F (assumption 8)
7. Cat-to-oil ratio

Order of Calculations

1. Calculation of Carbon and Hydrogen Rates

1.1 Feed rate in lb/h

$$\text{Feed(lb/h)} = \text{Feed(BPD)} * (\text{specific gravity}) * 350 / 24 \quad ...(1)$$

1.2 Carbon (C) rate in lb/h

$$\text{C(lb/h)} = \text{Feed(lb/h)} * \text{MAT coke(mass\% Feed)} / 100 \quad .....(2)$$

1.3 Dry air rate in lb/h from stoichiometric equation for carbon production from flue gas composition (mole%)

$$\text{Dry air (lb/h)} = \frac{\text{C(lb/h)} * \text{N2(mole\%)} * 3.03}{\text{CO2(mole\%)} + \text{CO(mole\%)}} \quad .....(3)$$

1.4 Hydrogen (H) rate in lb/h from stoichiometric equation using flue gas composition and dry air rate

$$\text{H(lb/h)} = \frac{\text{Dry air (lb/h)}}{\text{N2}} * \left[\frac{\text{N2}}{34.5} - \frac{\text{CO2} + \text{O2} + (\text{CO}/2)}{9.12}\right] \quad ...(4)$$

(Note: N2, CO2, O2, CO are all in mole%)

2. Calculation of Component Rates

2.1 Air rate in moles/h from (3) and molecular weight of air

Air(moles/h) = Air(lb/h) / 28.951.....(5)

2.2 Flue gas rate in moles/h from air rate and difference between amount of N2+Ar in air and flue gas

$$\text{Flue gas(moles/h)} = \frac{\text{Air(moles/h)} * \text{N2+Ar in air (mole\%)}}{\text{N2+Ar in flue gas(mole\%)}} \quad ...(6)$$

2.3 Rate of each component in flue gas (note: m.f. = mole fraction of component in flue gas = mole% / 100)

For each component:
Component(moles/h) = Component(m.f.) * Flue gas(moles/h)..(7)

3. Calculation of Coke Burning Rate, lb/h

3.1 Carbon and Hydrogen burning rates are known from (2) and (4). Sulfur burning rate can be calculated from its component rate in moles/h from (7) and its molecular weight (lb/mole)

S(lb/h) = S(moles/h) * 32.1.....(8)

3.2 Coke burning rate can be calculated from (2), (4), (8)

Coke(lb/h) = C(lb/h) + H(lb/h) + S(lb/h).....(9)

4. Calculation of Heat Liberated from Combustion of Coke

4.1 Heats of combustion for the various combustion routes are taken from the paper in Reference [13]. The assumptions used are also taken from this reference.

Combustion Route	Heat of Combustion, MMBTU/mole...(10)
C -> CO	0.0476
C -> CO_2	0.1693
S -> SO_2	0.1277
H -> H_2O	0.1040

4.2 Combustion rates are calculated for each combustion route (the component rate for H_2O = rate for H, which can be calculated from (4)). Component rates are from (7)

H_2O(moles/h) = H(moles/h)
= H(lb/h) / 2.02.....(11)

For each component:
Combust. rate(MMBTU/h) = Heat of Combust.(MMBTU/mole)
* Component rate(moles/h).....(12)

4.3 The total heat of combustion of coke is the sum of all the individual component rates determined in (12)

Heat of coke combust.(MMBTU/h) = sum of combust. rates...(13)

5. Calculation of Heat Contents of Coke and Air

5.1 Heat content of coke uses the coke burning rate determined in (9) and uses the specific heat capacity of coke found in Reference [13] of 0.5 BTU/lb-F

Coke heat(MMBTU/h) = coke rate(lb/h) * 0.5 BTU/lb-F
* (reactor temp(F) - datum temp(F)
/ 1 000 000.....(14)

5.2 Heat content of air uses the air rate from (5) and the specific heat capacity of air found in Reference [1] of 7.07 BTU/mole-F

Air heat(MMBTU/h) = air(moles/h) * 7.07 BTU/mole-F
* (air blower discharge temp(F)
- datum temp(F)) / 1 000 000.....(15)

6. Calculation of Total Heat to Regenerator

It is not necessary to calculate the heat content of the spent catalyst because this amount cancels the equivalent heat out with the regenerated catalyst [13]. The total heat to regenerator is the sum of the heat of combustion of coke (13), and the heat contents of the coke and the air (14), (15)

Heat to regen(MMBTU/h) = heat of coke combustion
+ coke heat + air heat.....(16)

7. Calculation of Heat to Catalyst

7.1 The majority of the heat loss is the flue gas heat. To calculate this, the flue gas temperature must be known, and the flue gas temperature is dependent on the regenerator temperature, which is the variable being calculated. As stated in the assumptions, the total heat losses are assumed to be 35% of the total heat to the regenerator.

Heat losses(MMBTU/h) = heat to regen(MMBTU/h) * 0.35.....(17)

7.2 Since the regenerator is in heat balance, the total heat out must equal the total heat in. The heat to catalyst is the heat in minus the losses in (17)

Heat to catalyst(MMBTU/h) = heat to regen - heat losses...(18)
Heat to cat(BTU/h) = heat to cat(MMBTU/h) * 1 000 000.....(19)

8. Calculation of Regenerator Temperature

8.1 The catalyst circulation rate (CCR) is calculated from the feed rate (1) and the cat-to-oil ratio

CCR(lb/h) = feed(lb/h) * cat/oil.....(20)

8.2 The heat capacity of the catalyst was taken from Reference [13] as 0.265 BTU/lb-F. The regenerator temperature was assumed to be the regenerator dense phase temperature mentioned in Reference [13]. The following equation is used to calculate the heat to catalyst (already determined in (19) from the CCR and regen and reactor temperatures

Heat to cat(BTU/h) = CCR(lb/h) * 0.265 BTU/lb-F
* (regen temp(F) - reactor temp(F))..(21)

Rearranging (21)

$$\text{Regen temp(F)} = \frac{\text{heat to cat(BTU/h)}}{\text{CCR(lb/h)} * 0.265\ \text{BTU/lb-F}} + \text{reactor temp(F)} \quad \ldots.(22)$$

An alternate method for estimating regenerator temperature is outlined in a recent publication by Murphy and Cheng, where an algorithm is given for their calculation [14].